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Metal-free synthesis of 1,1-dimethyl-2,2,2-trifluoroethyl substituted quinazolinones via tandem radical cyclization of quinazolin-4(3*H*)-ones with 3,3,3-trifluoro-2,2-dimethylpropanoic acid

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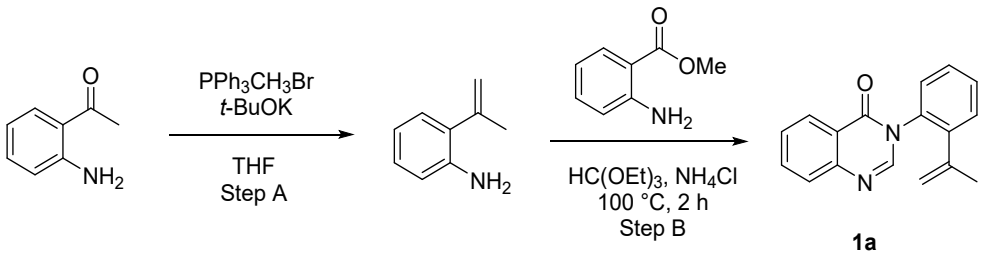
I. General information

Unless specifically mentioned otherwise, solvents and reagents were procured from commercial suppliers. The purification of products was carried out through silica gel column chromatography. ^{1}H NMR spectra were recorded at frequencies of 400, 500, or 600 MHz using Bruker instruments, while ^{13}C NMR spectra were captured at 101, 126, or 151 MHz with Bruker equipment. The chemical shifts for ^{1}H and ^{13}C NMR were referenced to internal Me4Si at 0 ppm. Notations such as br (broad), s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), and dd (doublet of doublet) were employed. Melting points were determined utilizing a WRS-1B melting point apparatus from Shanghai Shen Guang Instrument Co., Ltd., Shanghai, China.

II. General procedure

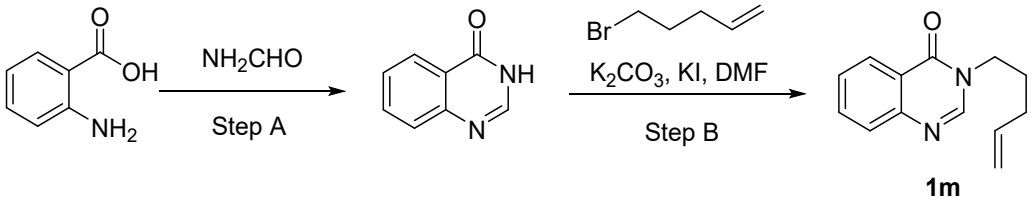
(a) Synthesis of conjugated quinazoline-4(3*H*)-one derivatives 1 (1a as an example) [1]



Step A: Synthesis of 2-(prop-1-en-2-yl) aniline: To a 250 mL oven-dried round-bottom flask was charged with methyltriphenylphosphonium bromide (10.72 g, 30 mmol) and THF (30 mL) under nitrogen atmosphere, followed by the addition of potassium tert-butoxide (3.36 g, 30 mmol) at 0 °C. The reaction mixture was allowed to warm to ambient temperature and stir for 30 minutes. Next, 2-aminoacetophenone (2.42 g, 10 mmol) was added. The reaction mixture was stirred at room temperature overnight. After completion, the reaction was quenched with water, and extracted with ethyl acetate (100 mL). The organic phase was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The reaction mixture was purified via flash column chromatography on silica gel to give 2-(prop-1-en-2-yl)aniline as a colorless oil.

Step B: Synthesis of quinazoline-4(3*H*)-one derivative 1a: A mixture of 2-amino-benzoic acid esters (2.5 mmol), 2-(prop-1-en-2-yl) aniline (3.0 mmol), ortho esters (3.8 mmol) and NH_4Cl (1.0 mmol) was heated with stirring at 100 °C for 2 h. After cooling to room temperature, water was added, and the product was extracted with ethyl acetate (2×30 mL). The organic layer was dried with anhydrous Na_2SO_4 and filtered. The filtrate was concentrated in vacuo. The crude product was purified by flash column chromatography on silica gel (PE:EA = 8:1) to afford quinazoline-4(3*H*)-one derivative **1a** as a white solid.

(b) Synthesis of quinazoline-4(3*H*)-one derivatives 1 (1m as an example) [2]

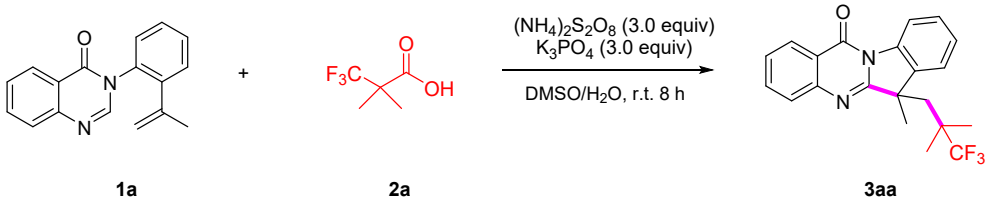


Step A: Synthesis of quinazoline-4(3*H*)-one: To a 10 mL round-bottomed flask equipped with a stir bar were added anthranilic acid (1.37g, 10 mmol) and formamide (4.0 mL, 100 mmol). The reaction mixture was stirred at 130 °C for 4 h. After full consumption of anthranilic acid, the reaction mixture was cooled to room temperature and then poured into icy water. The resultant light precipitates were filtered and washed three times with water (100 mL) and dried over vacuum to give quinazoline-4(3*H*)-one, which was used for the next step without further purification.

Step B: Synthesis of quinazoline-4(3*H*)-one derivative 1n: A 150 mL round-bottom flask equipped with a magnetic stirrer bar was charged with quinazolin-4(3*H*)-one (731mg, 5 mmol), potassium carbonate (1.38g, 10 mmol), and DMF (50 ml). The resulting mixture was heated to 80 °C with stirring for 30 min. After that, KI (83, 5 mmol) was added and after stirring for further 15 min, brominated olefins (711μL, 6 mmol) diluted with DMF (7 mL) was dropwise added into the mixture. The reaction mixture was heated to 60 °C in an oil bath and stirred for 3 h. After the reaction

completed, the resulting mixture was cooled to room temperature. The reaction mixture was washed with water and extracted with ethyl acetate three times. The combined organic layer was washed with brine, dried with anhydrous Na_2SO_4 and evaporated, and the residue was purified through flash column chromatography on silica gel to afford desired product **1a** as a white solid.

(c) General procedure for the synthesis of desired products 3 (3a as an example)

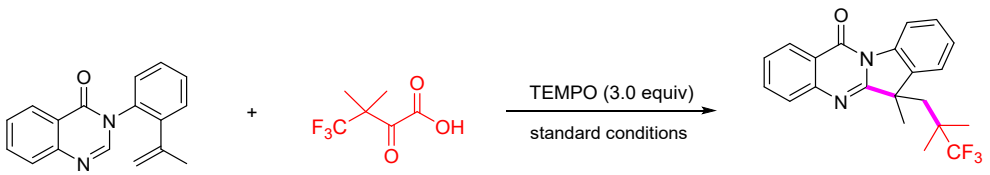


1a **2a** **3aa**

In a nitrogen atmosphere, 3-(2-(prop-1-en-2-yl)phenyl)quinazolin-4(3*H*)-one (**1a**) (0.2 mmol, 52.4 mg), 3,3,3-trifluoro-2,2-dimethylpropanoic acid (**2a**) (0.6 mmol, 93.7 mg), $(NH_4)_2S_2O_8$ (0.6 mmol, 136.8 mg), and DMSO/H_2O (v/v=4/1, 2 mL) were added to a Schlenk flask. The reaction mixture was stirred at 80°C for 8 hours. After complete consumption of the starting material **1a**, 10 mL of saturated potassium carbonate solution was added. The mixture was extracted with ethyl acetate (10 mL × 3), and the solvent was removed under vacuum. Flash column chromatography using a mixture of Petroleum ether and ethyl acetate as the eluent was employed to purify the residue, yielding the desired product **3aa** with an 77% yield.

III. Mechanistic Studies

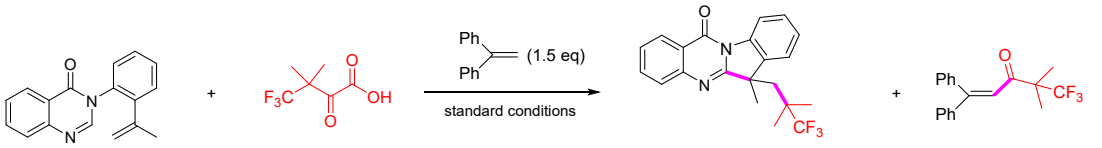
(a) Radical-trapping experiment using TEMPO as the radical scavenger



1a **2a** **3aa**, 0%

In a nitrogen atmosphere, 3-(2-(prop-1-en-2-yl)phenyl)quinazolin-4(3H)-one (**1a**) (0.2 mmol, 52.4 mg), TEMPO (93.8 mg, 0.6 mmol), 3,3,3-trifluoro-2,2-dimethylpropanoic acid (**2a**) (0.6 mmol, 93.7 mg), $(NH_4)_2S_2O_8$ (0.6 mmol, 136.8 mg), and DMSO/H_2O (v/v=2/1, 2 mL) were added to a Schlenk flask. The reaction mixture was stirred at 80°C for 8 hours. The progress of the reaction was monitored by TLC. After the specified time, no corresponding product **3aa** was formed by TLC analysis.

(b) Control reaction using 1,1-diphenylethylene as the radical-trapping reagent



1a **2a** **3aa**, 0% **5**, 28% detected by LC-MS

In a nitrogen atmosphere, 3-(2-(prop-1-en-2-yl)phenyl)quinazolin-4(3H)-one (**1a**) (0.2 mmol, 52.4

mg), 1,1- diphenylethylene (106.4 μL, 0.6 mmol), 2-oxo-2-(phenylamino)acetic acid (**2a**) (0.6 mmol, 93.7 mg), $(NH_4)_2S_2O_8$ (0.6 mmol, 136.8 mg), and DMSO/H_2O (v/v=2/1, 2 mL) were added to a Schlenk flask. The reaction mixture was stirred at 80°C for 8 hours. After completion of the reaction, the resulting mixture was analyzed by GC-MS. No corresponding product **3aa** was detected and the heck-type product **5** was isolated in 28% yield.

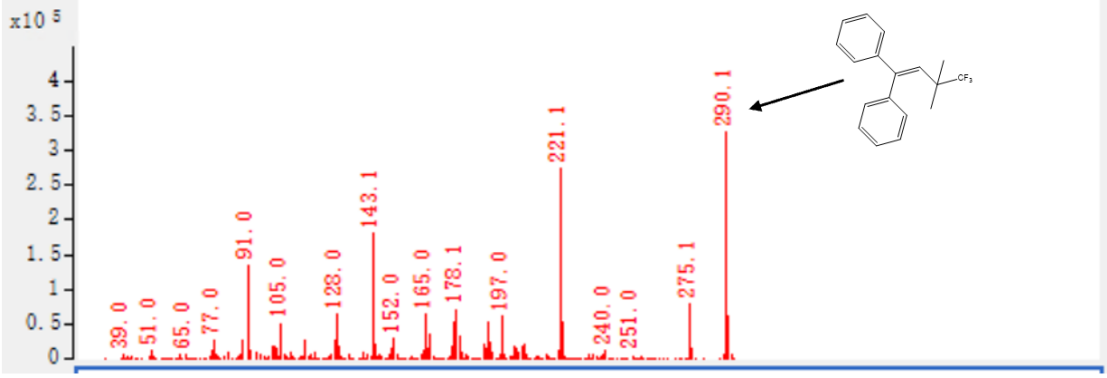
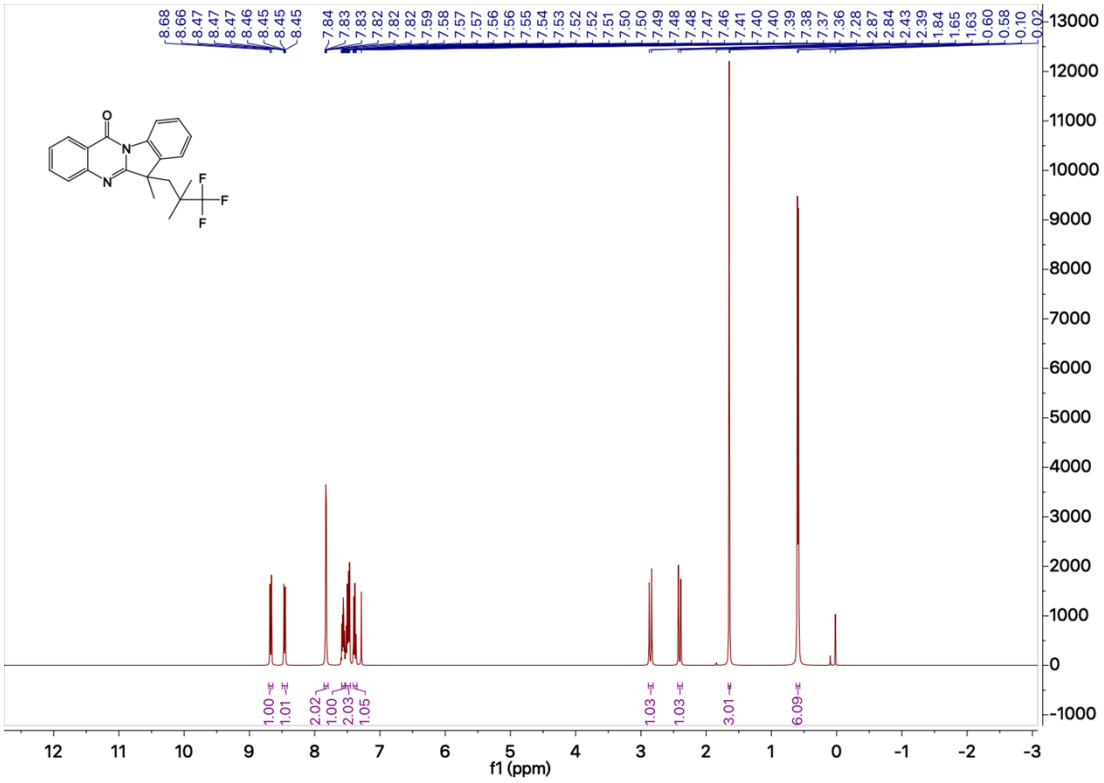


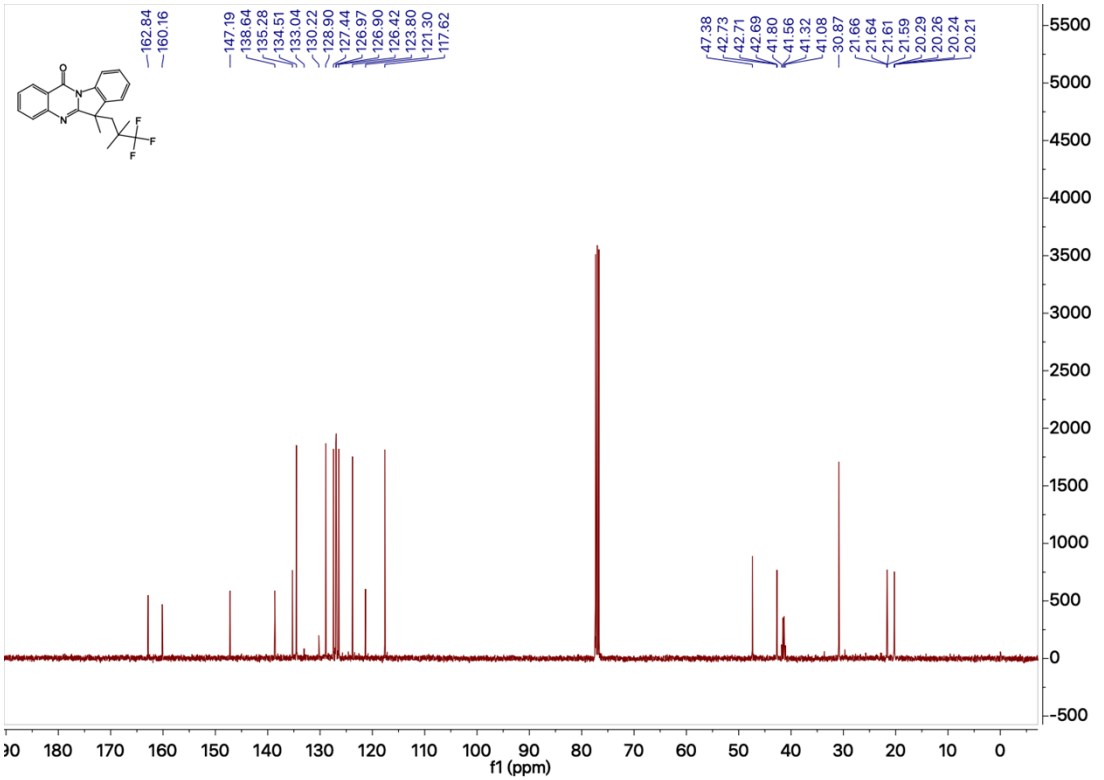
Figure S1: Radical trapping experiment

IV. NMR spectra of Products

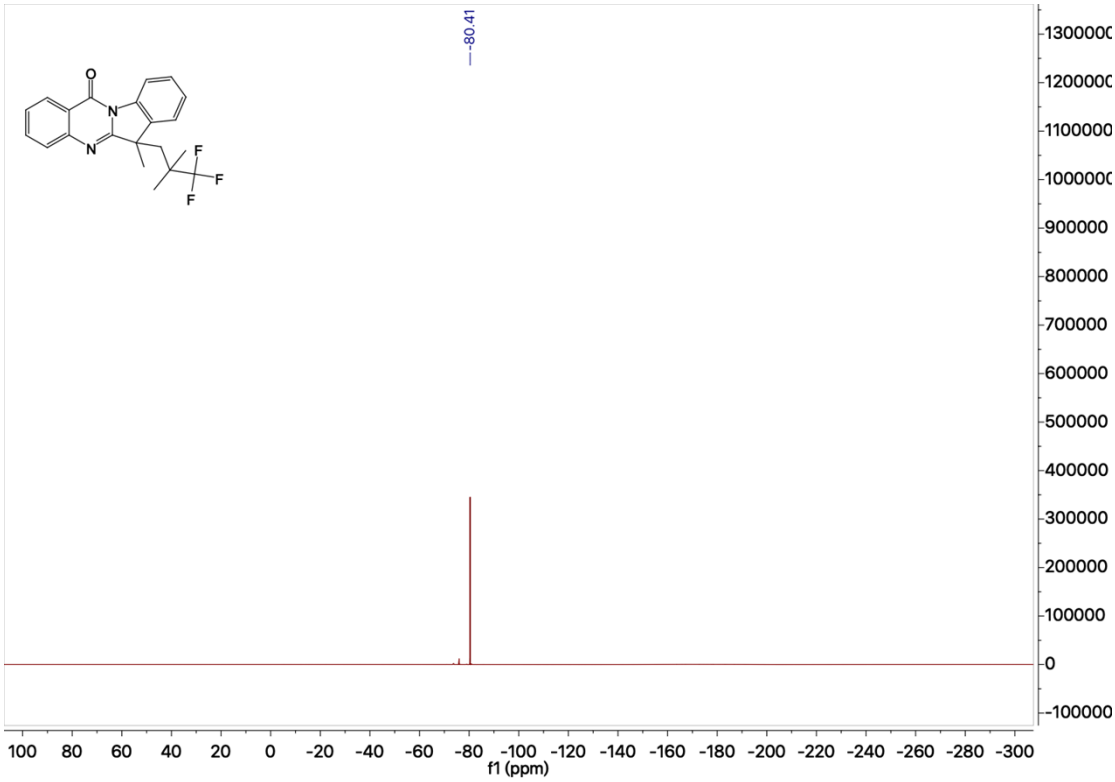
3aa ^{1}H Chloroform-*d*, 400 MHz



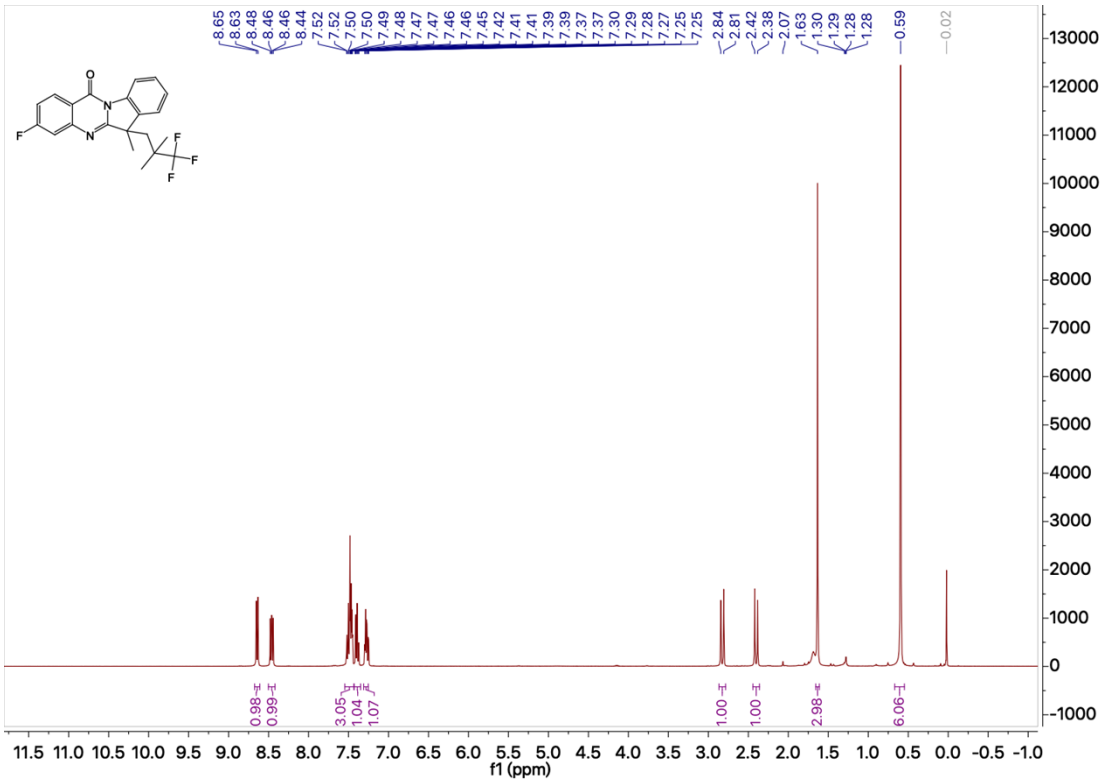
3aa ^{13}C Chloroform-*d*, 101 MHz



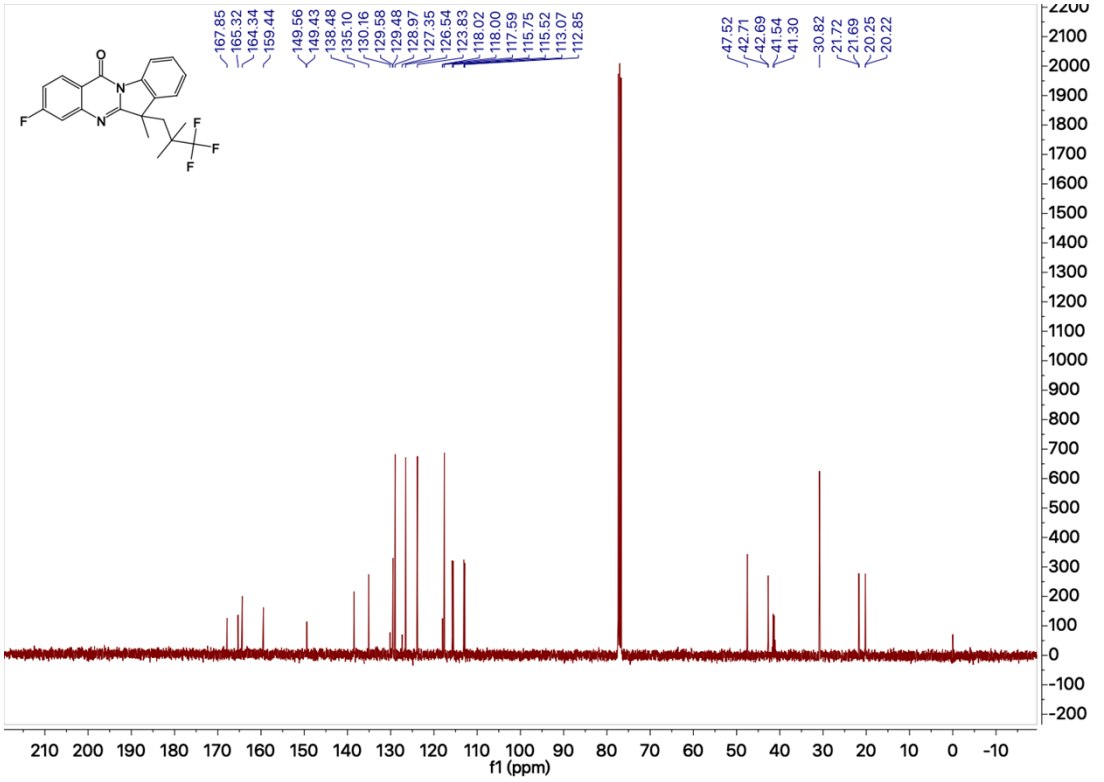
3aa ^{19}F Chloroform-*d*, 376 MHz



3ab ^{1}H Chloroform-*d*, 400 MHz



3ab ^{13}C Chloroform-*d*, 101 MHz



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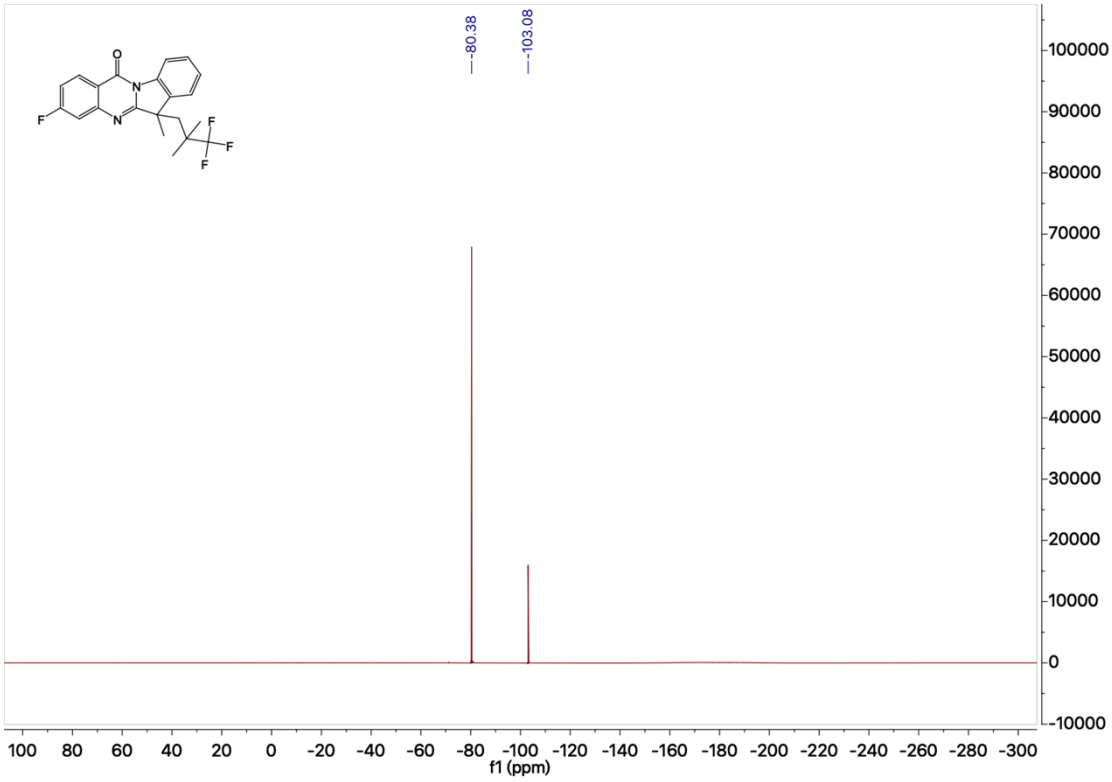
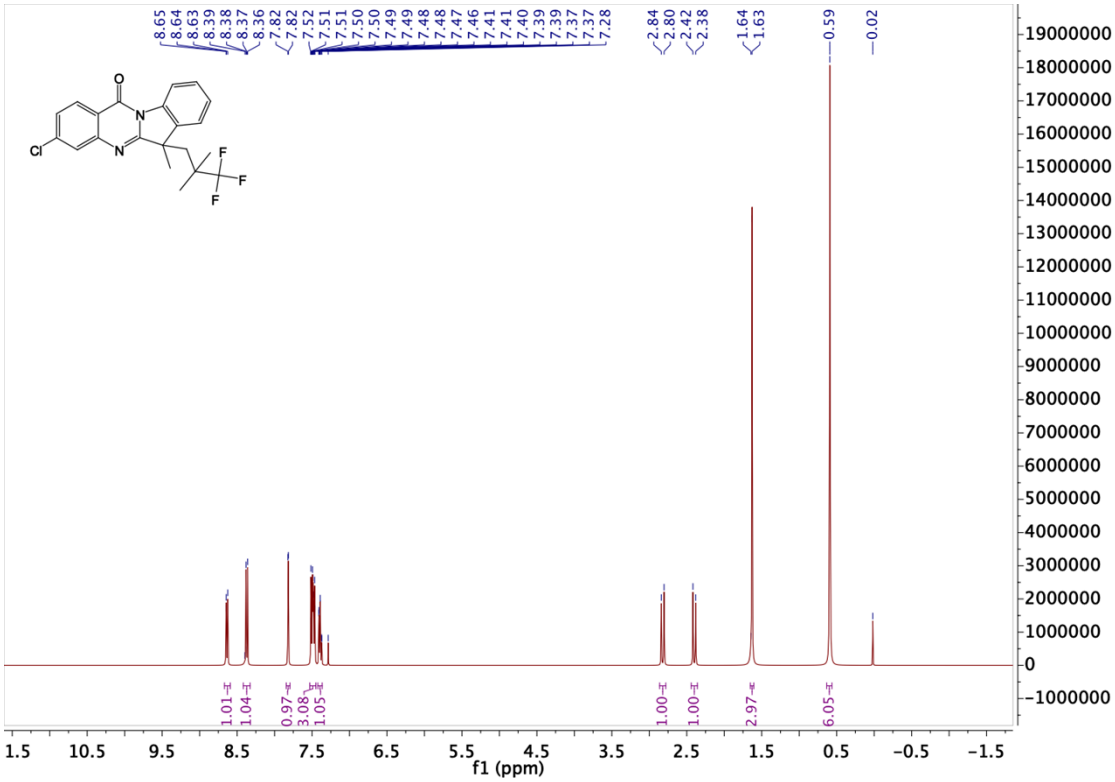
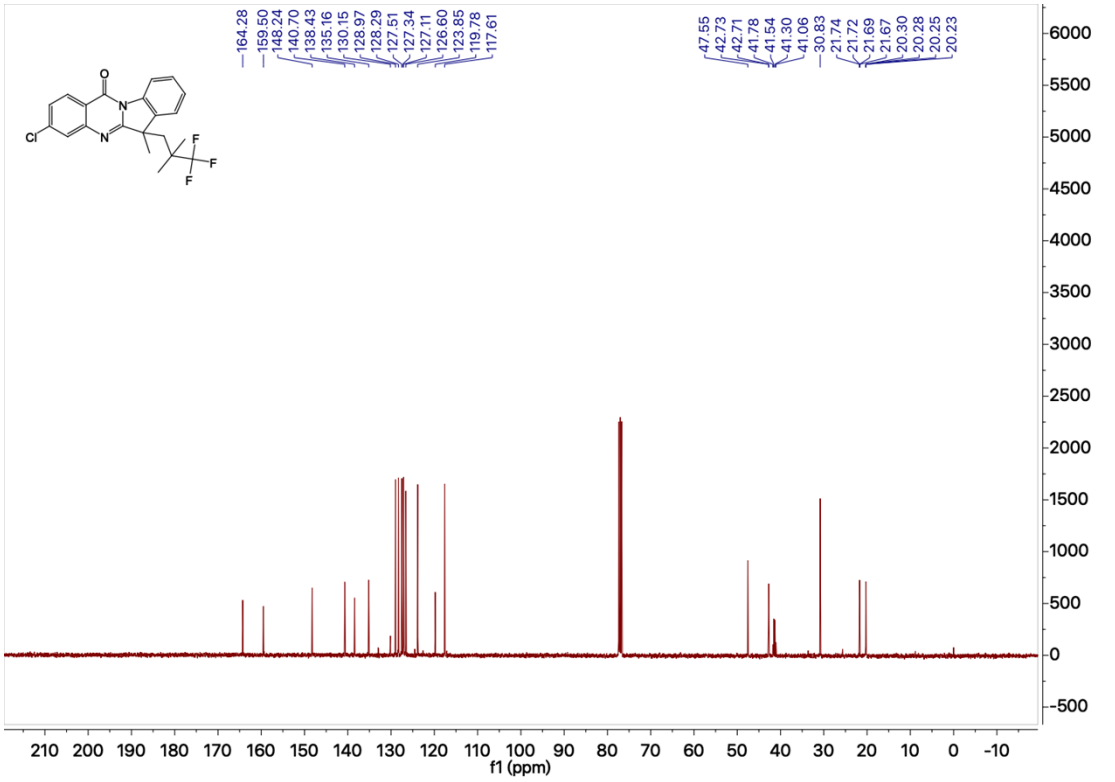


3ac ^{1}H Chloroform-*d*, 400 MHz



3ac ^{13}C Chloroform-*d*, 101 MHz



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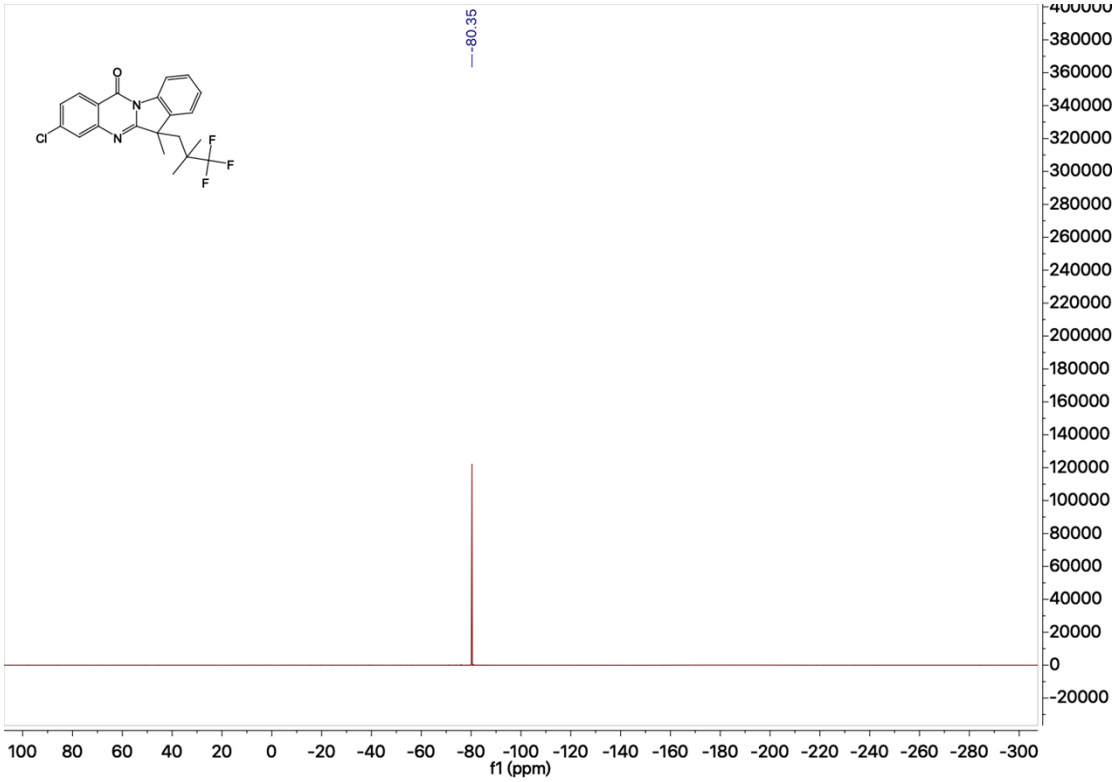
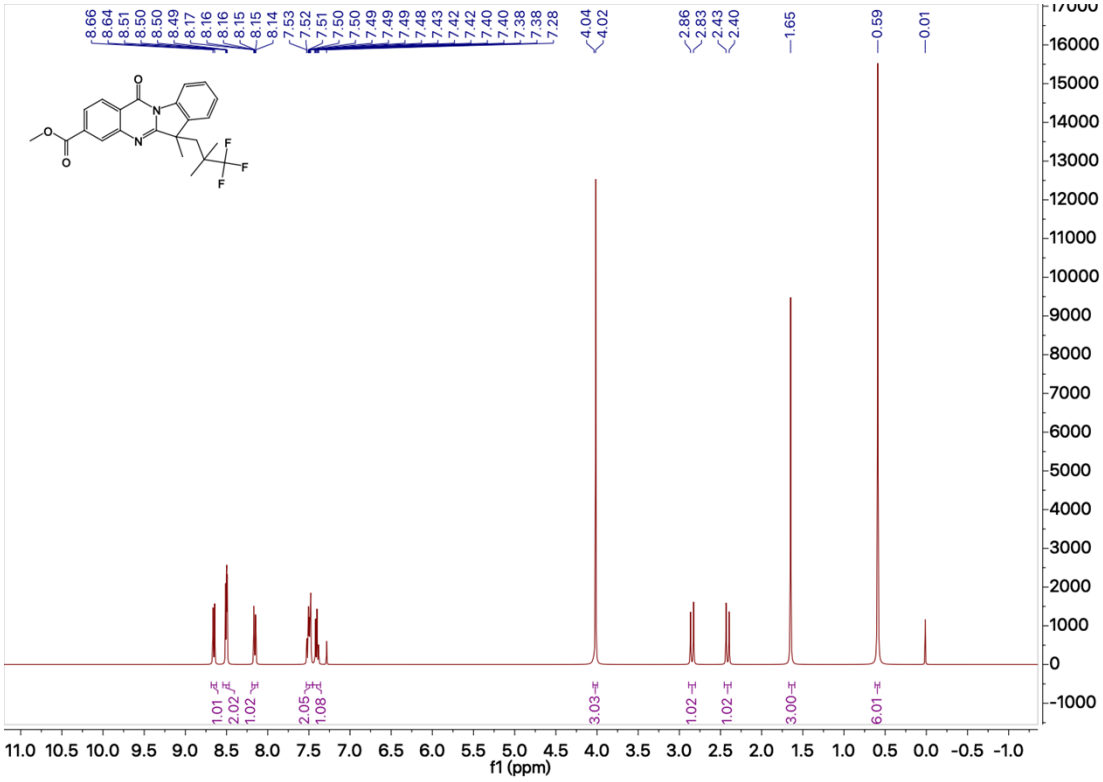


3ae ^{1}H Chloroform-*d*, 400 MHz



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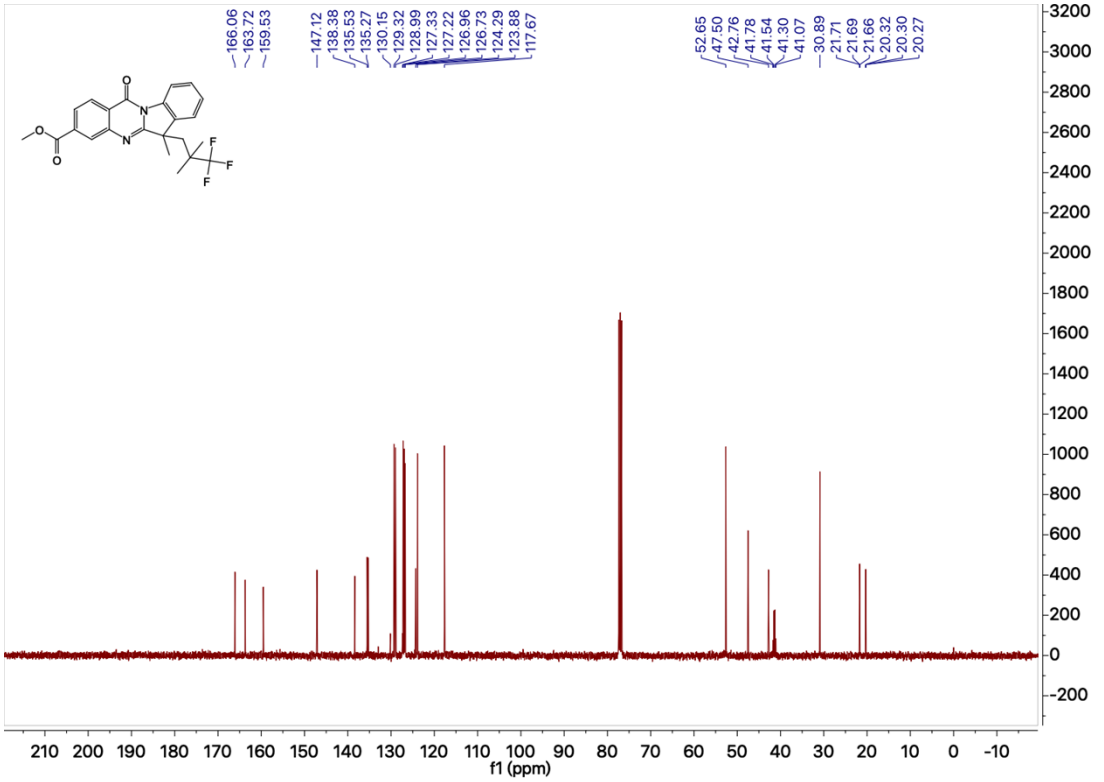

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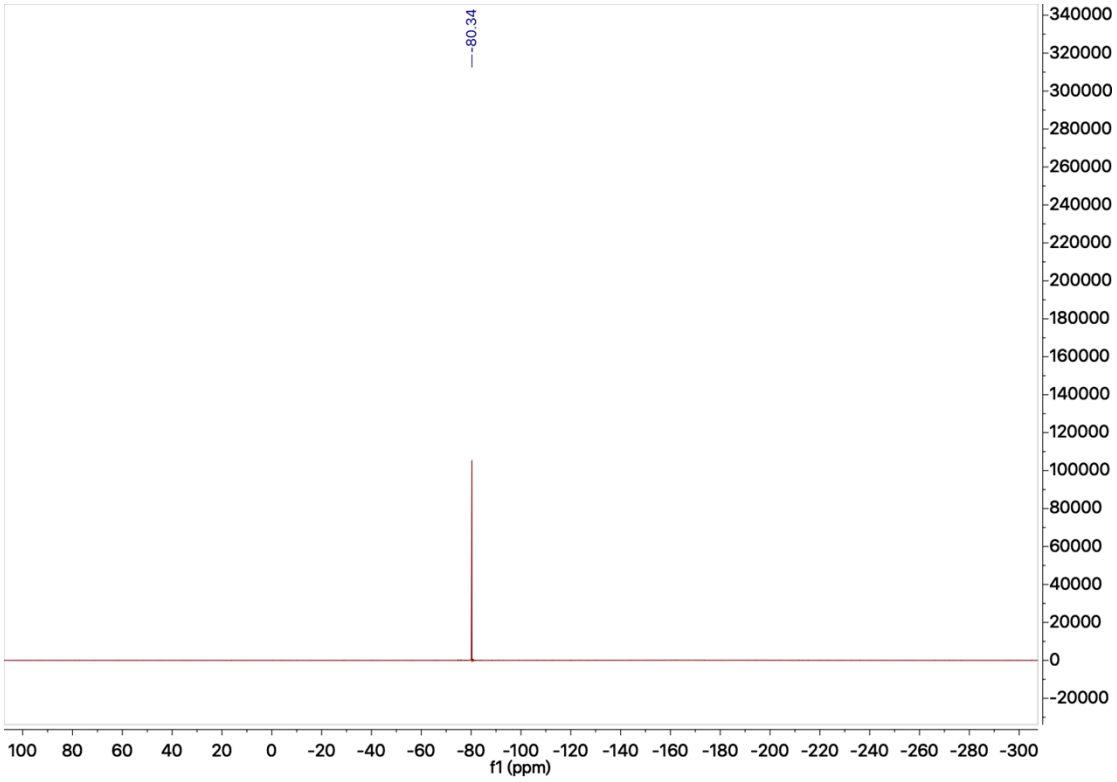

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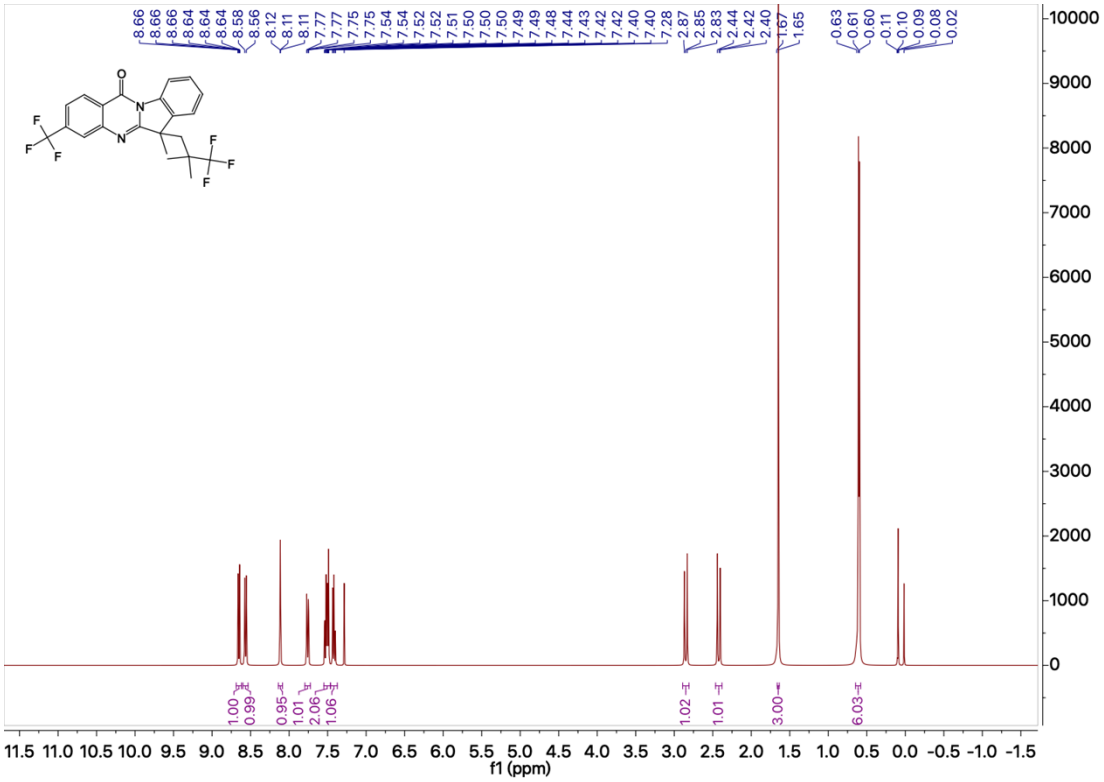

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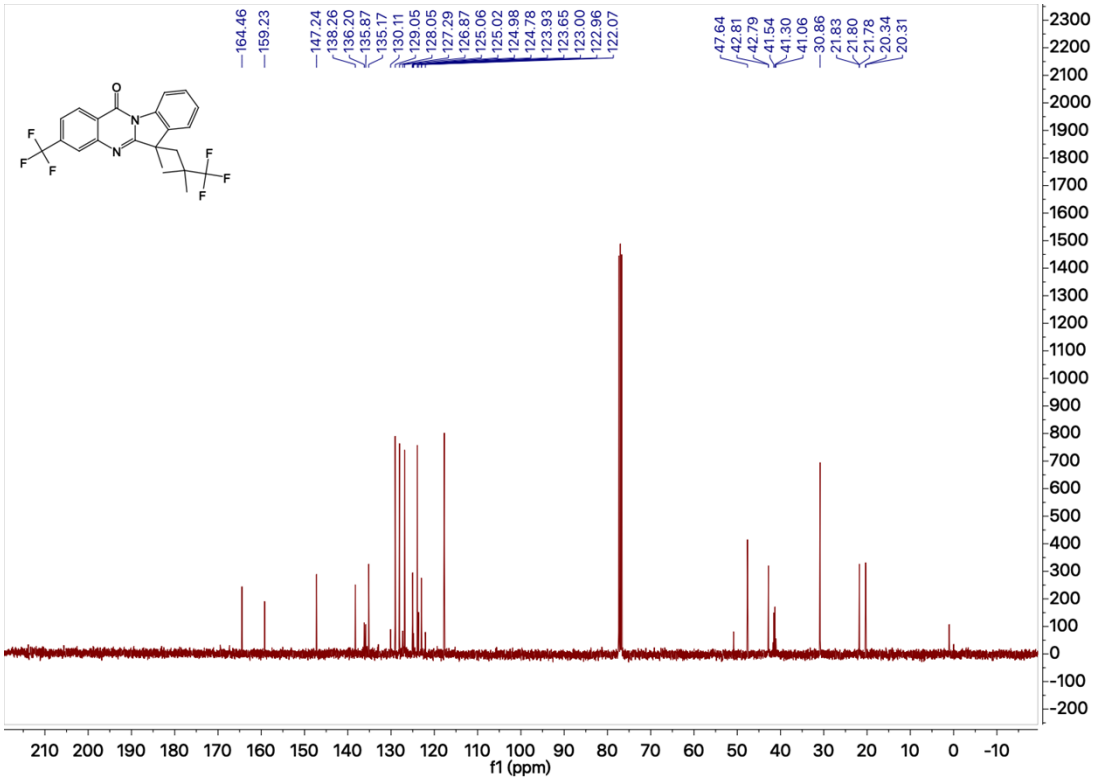

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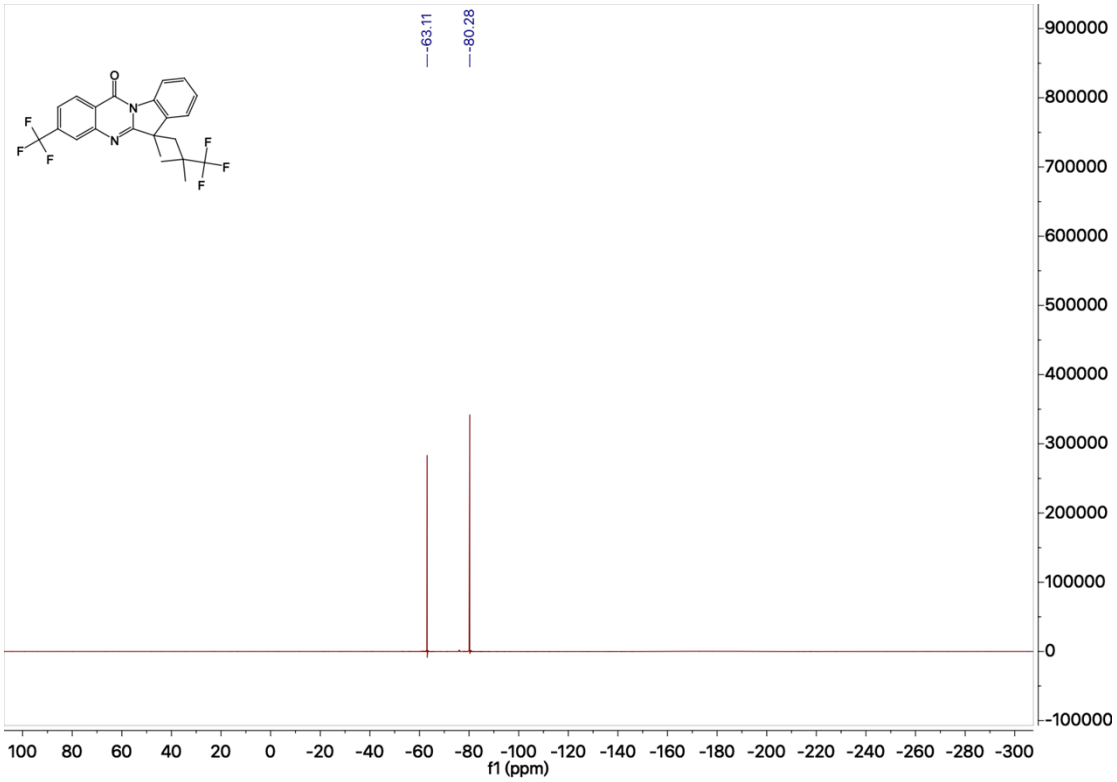

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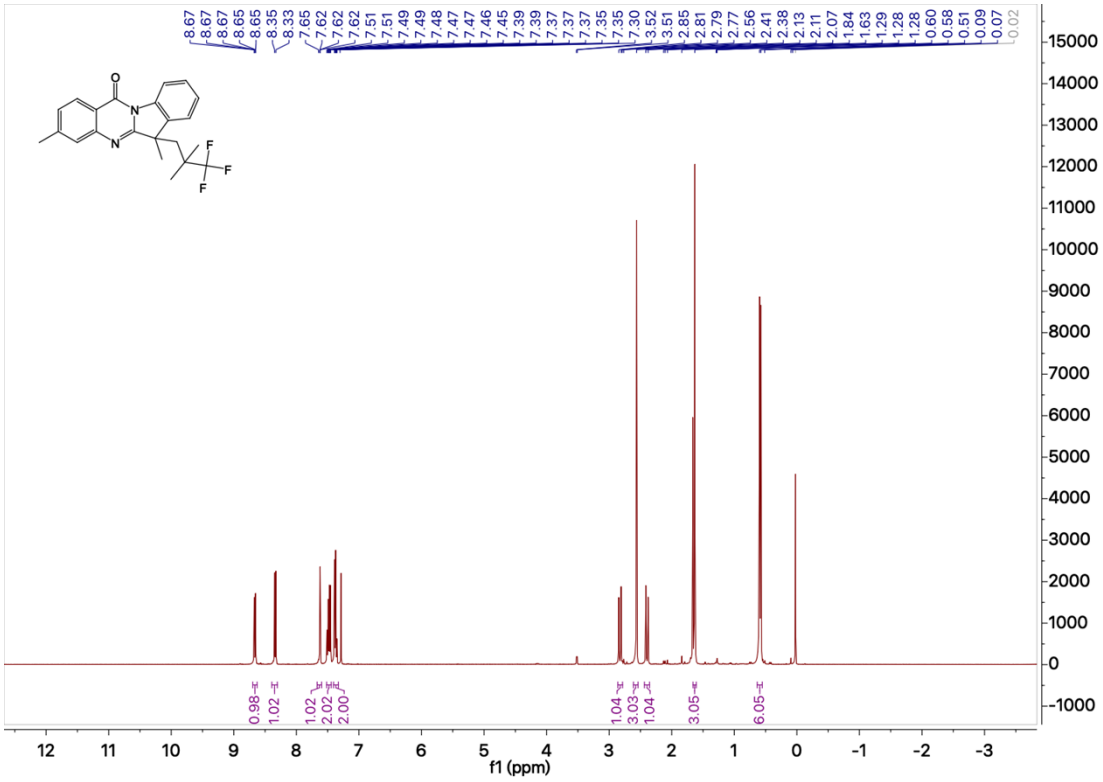

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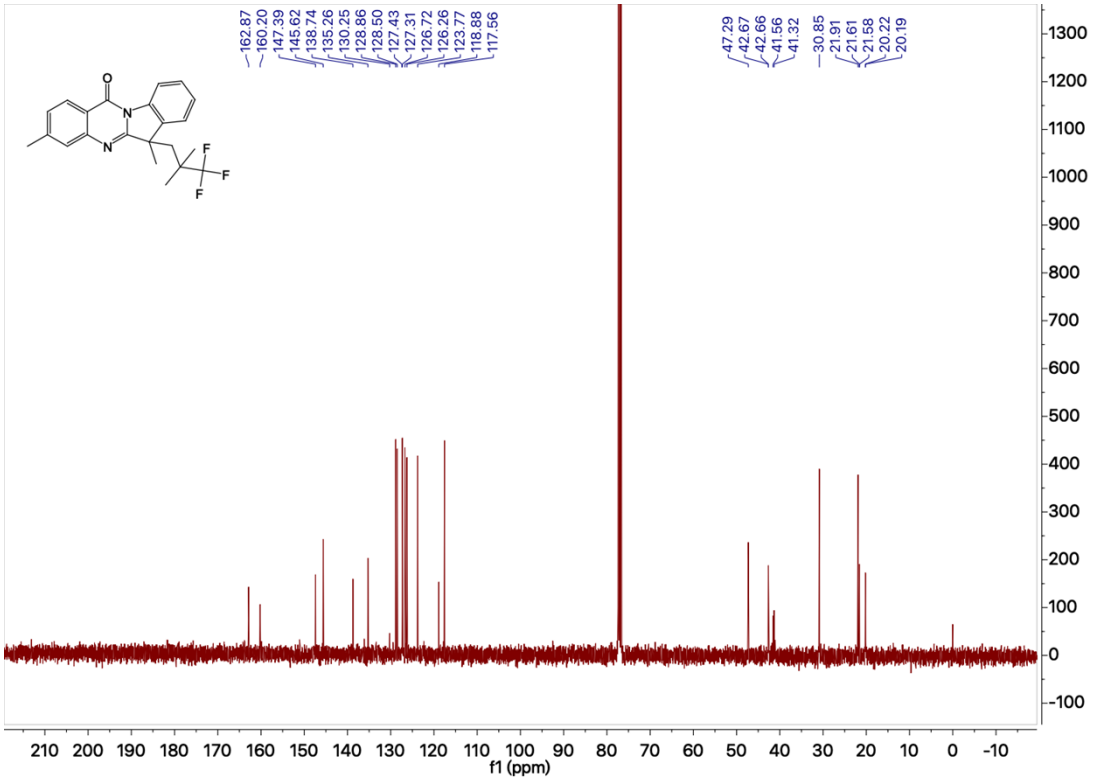

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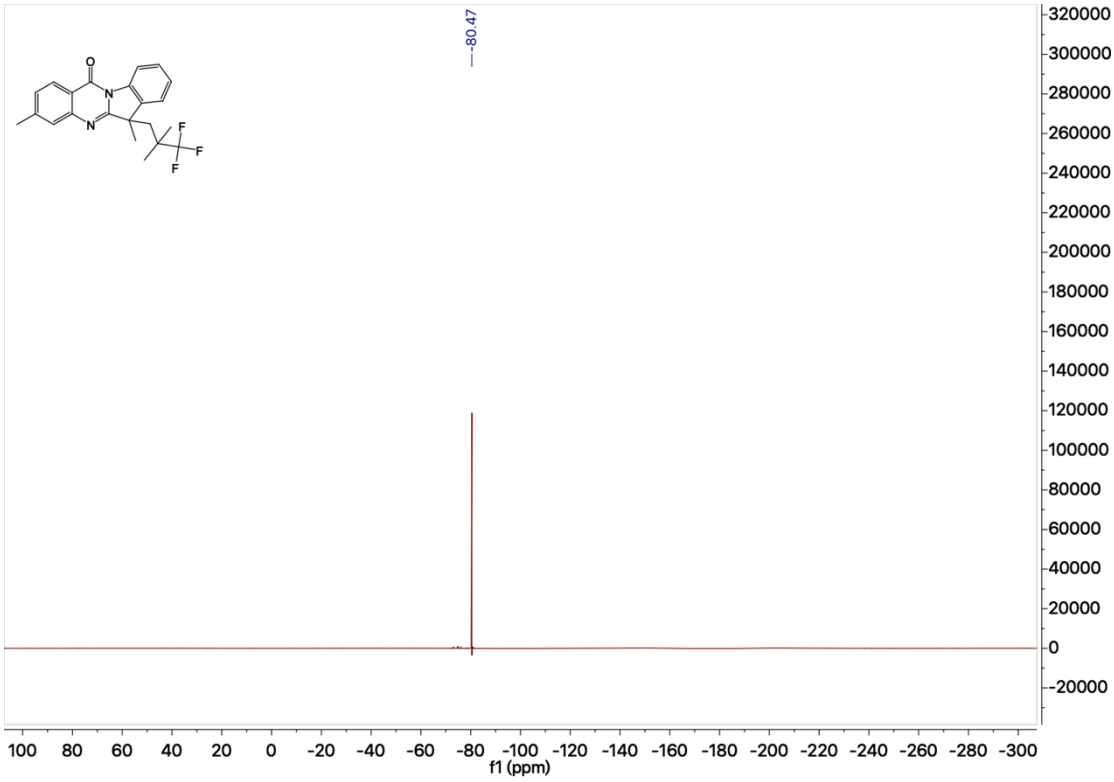

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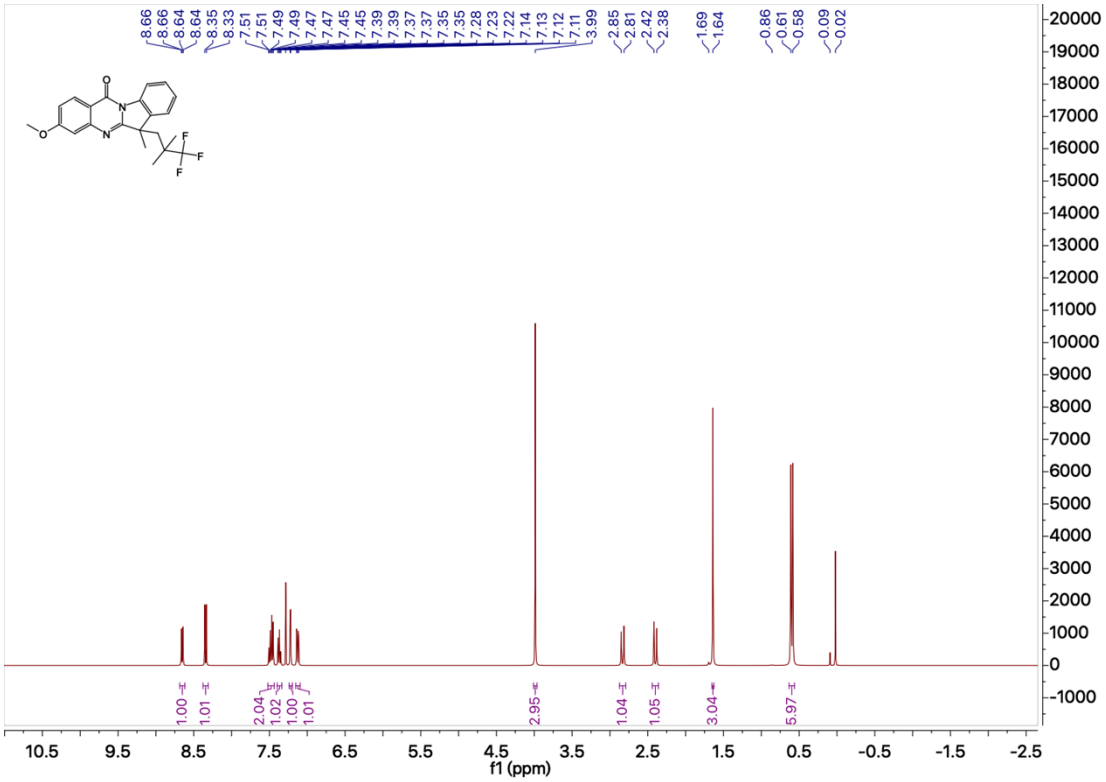

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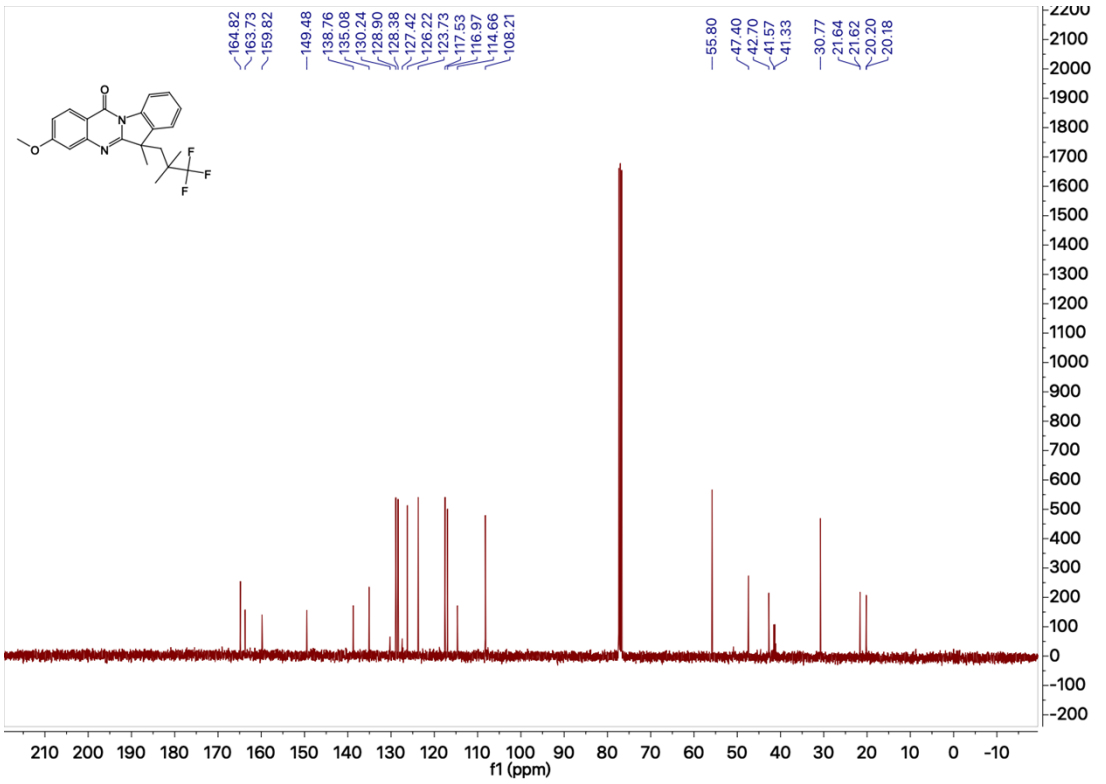

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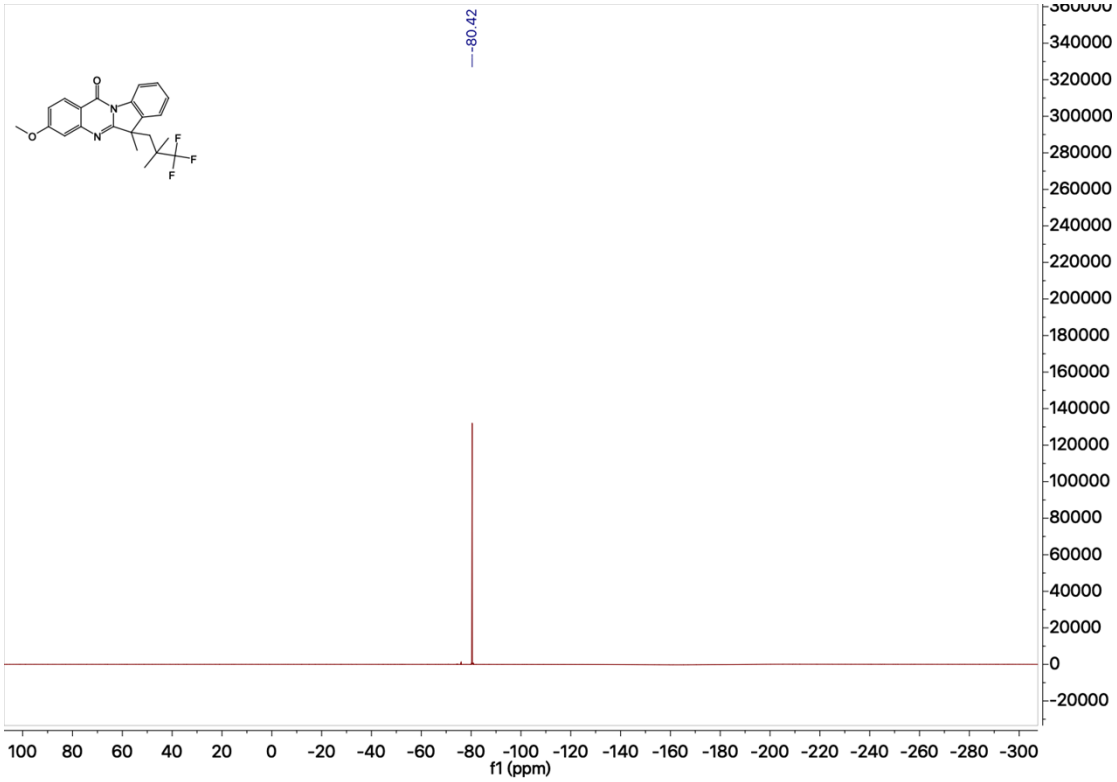

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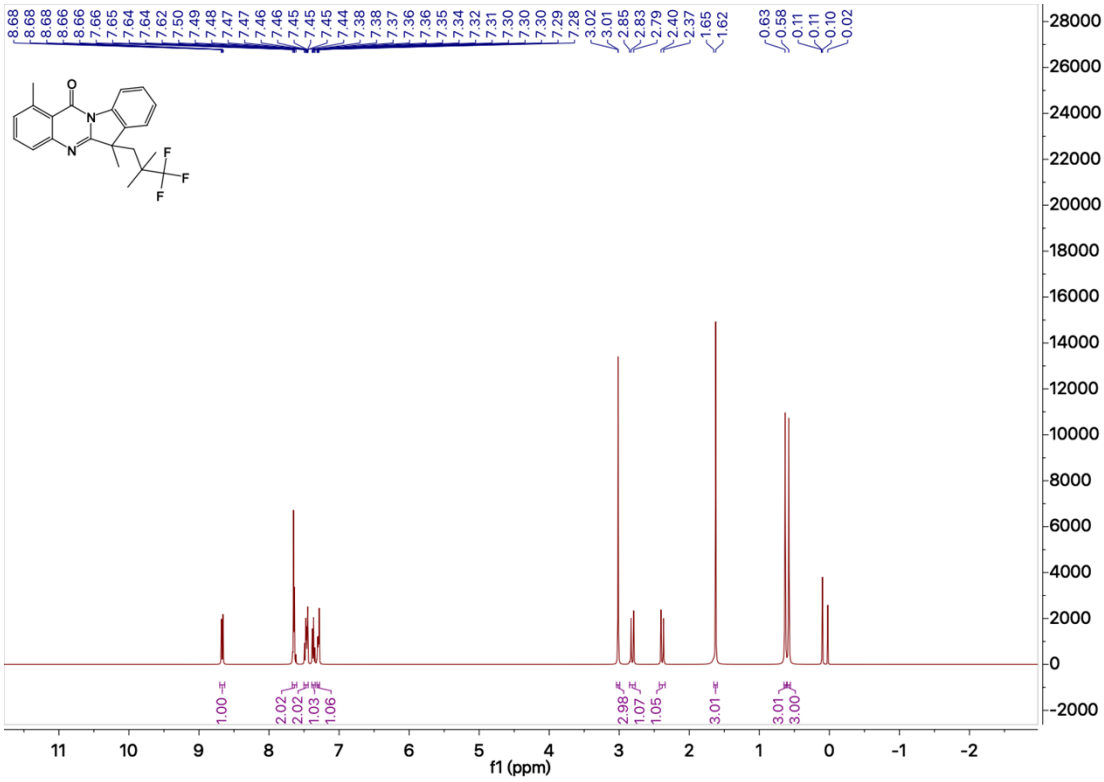

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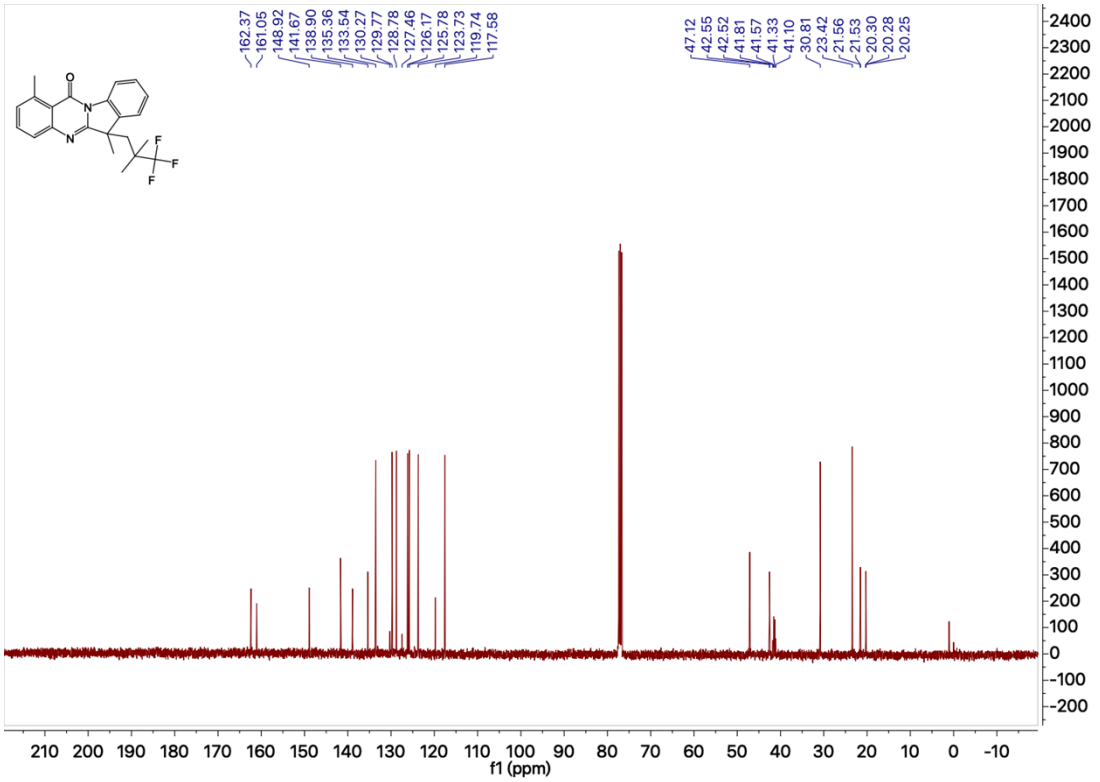

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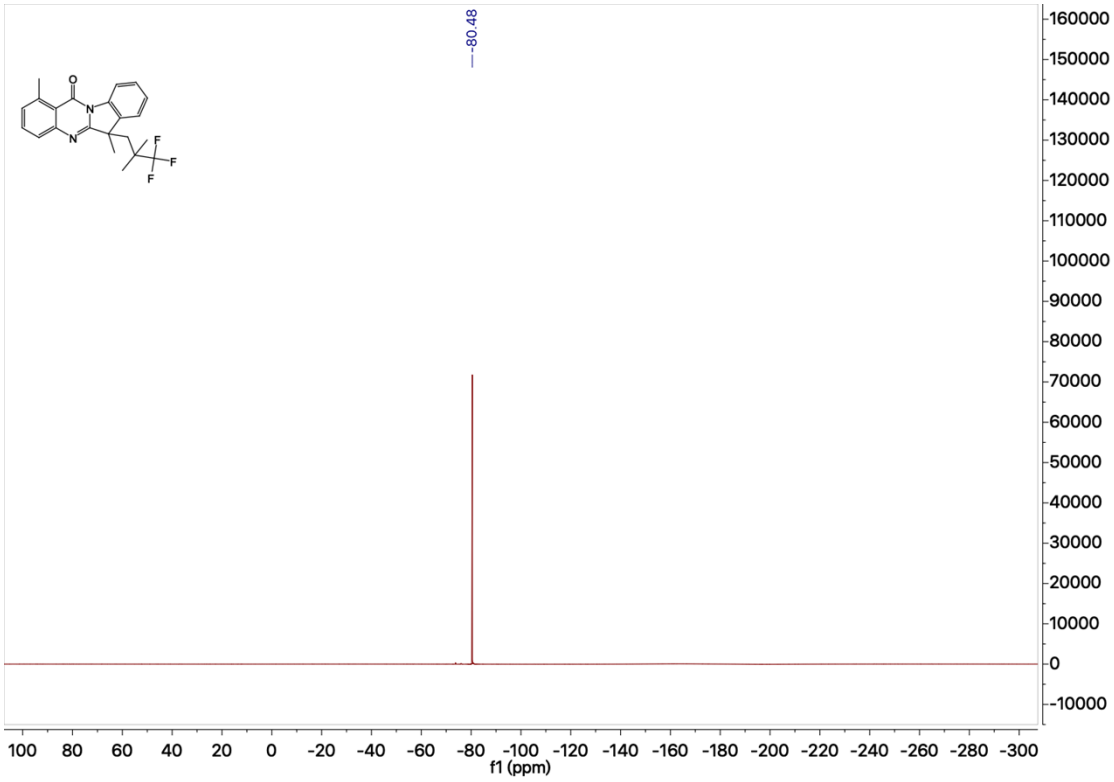

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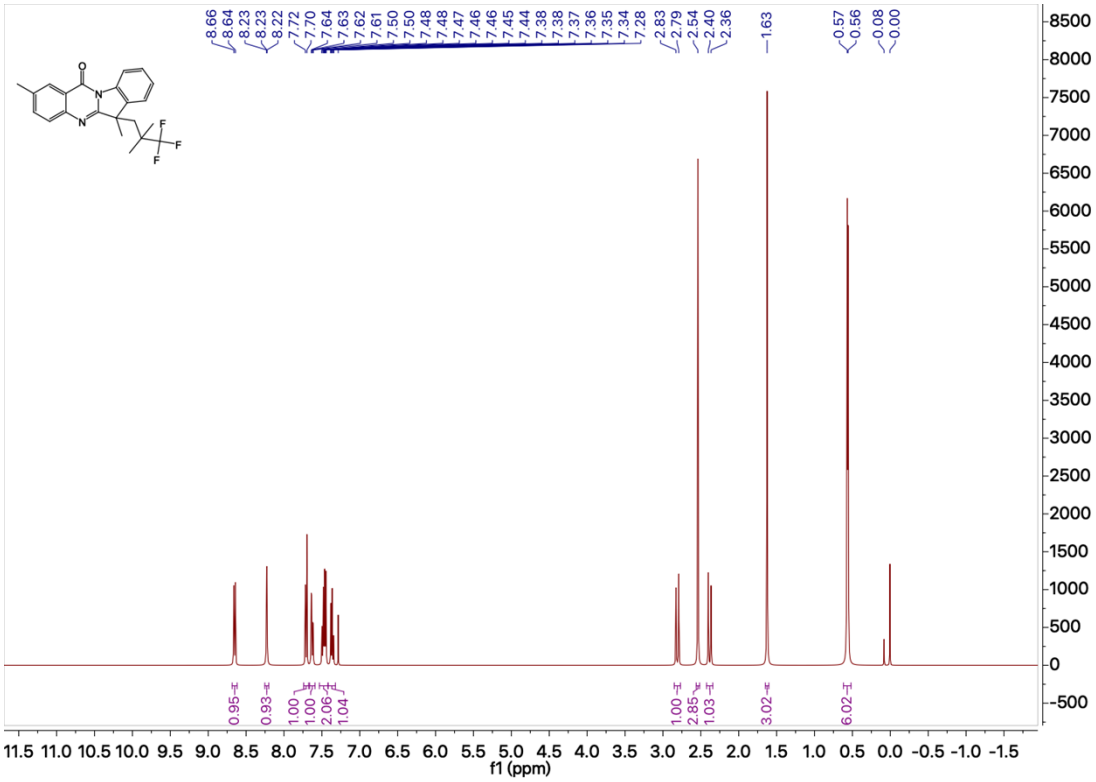

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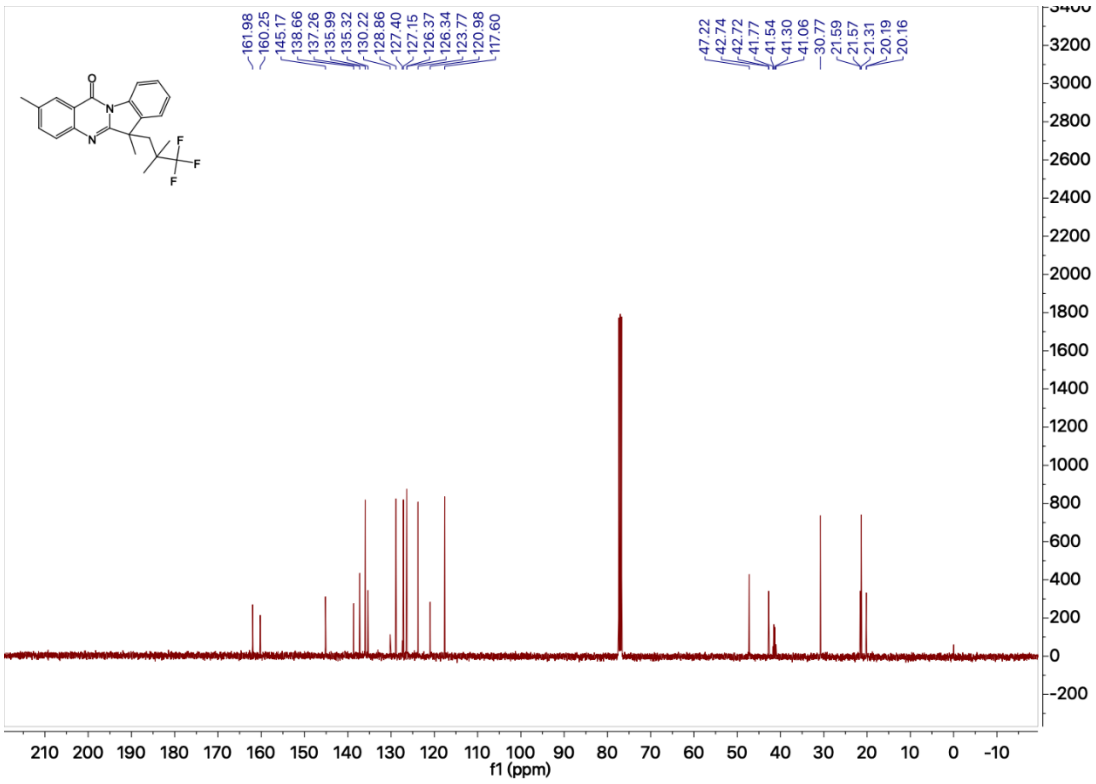

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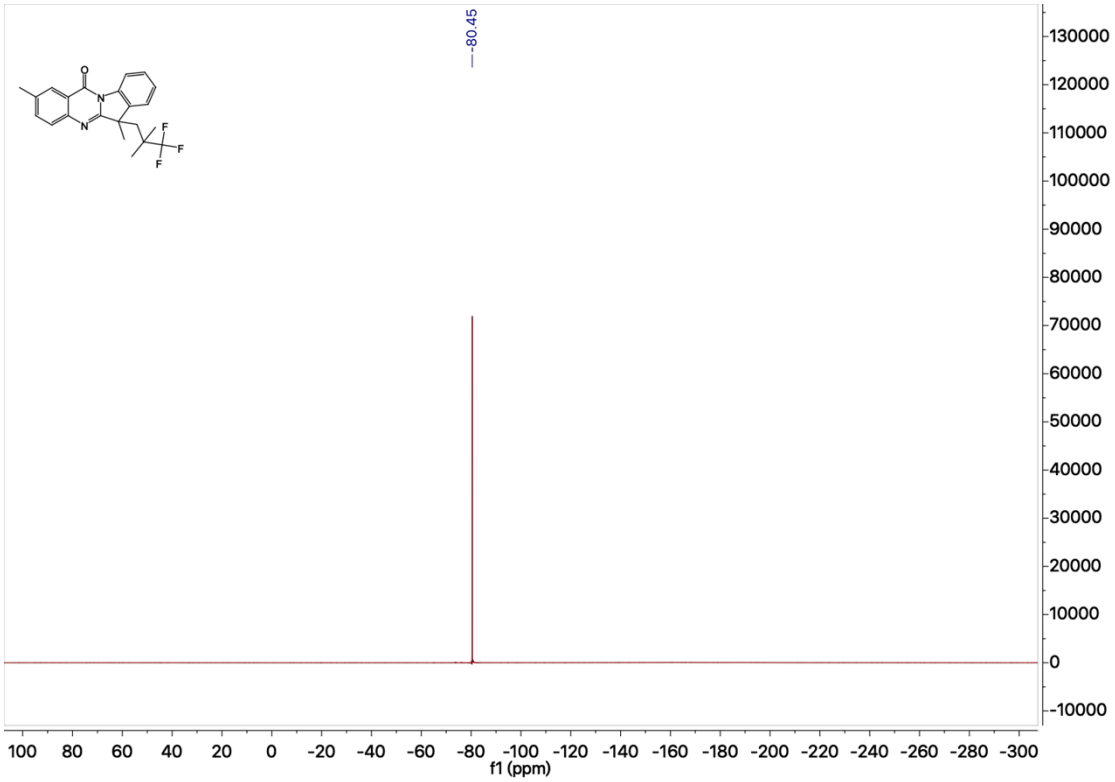

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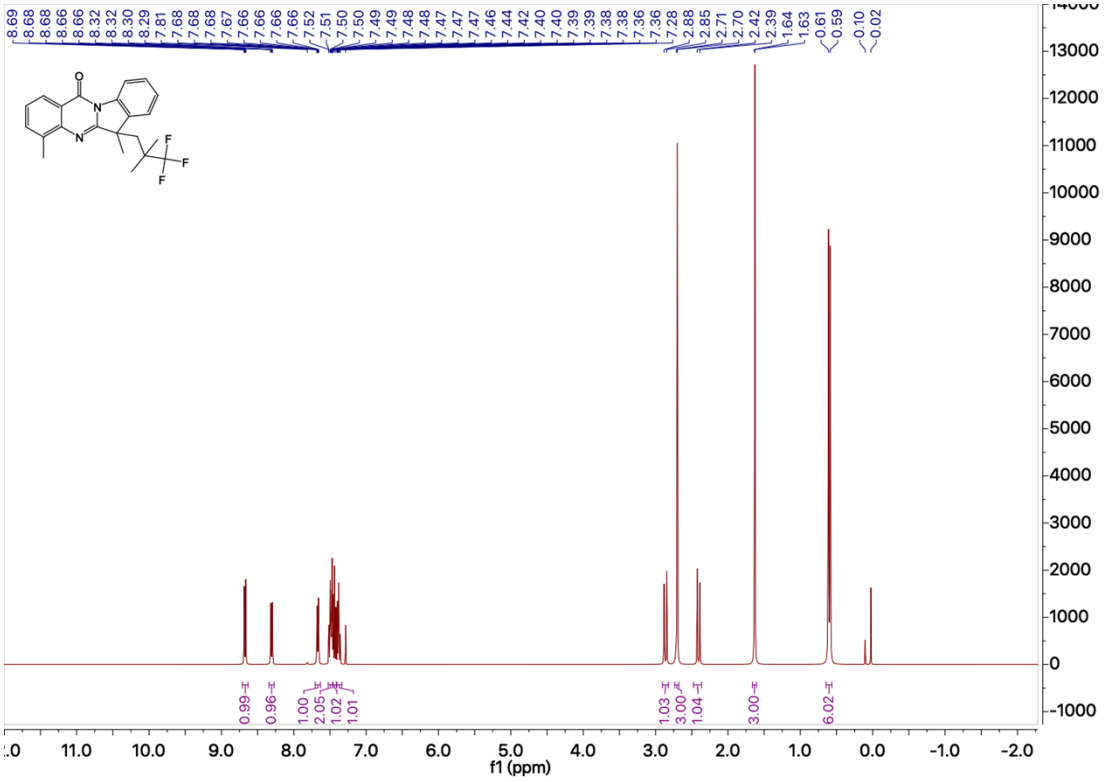

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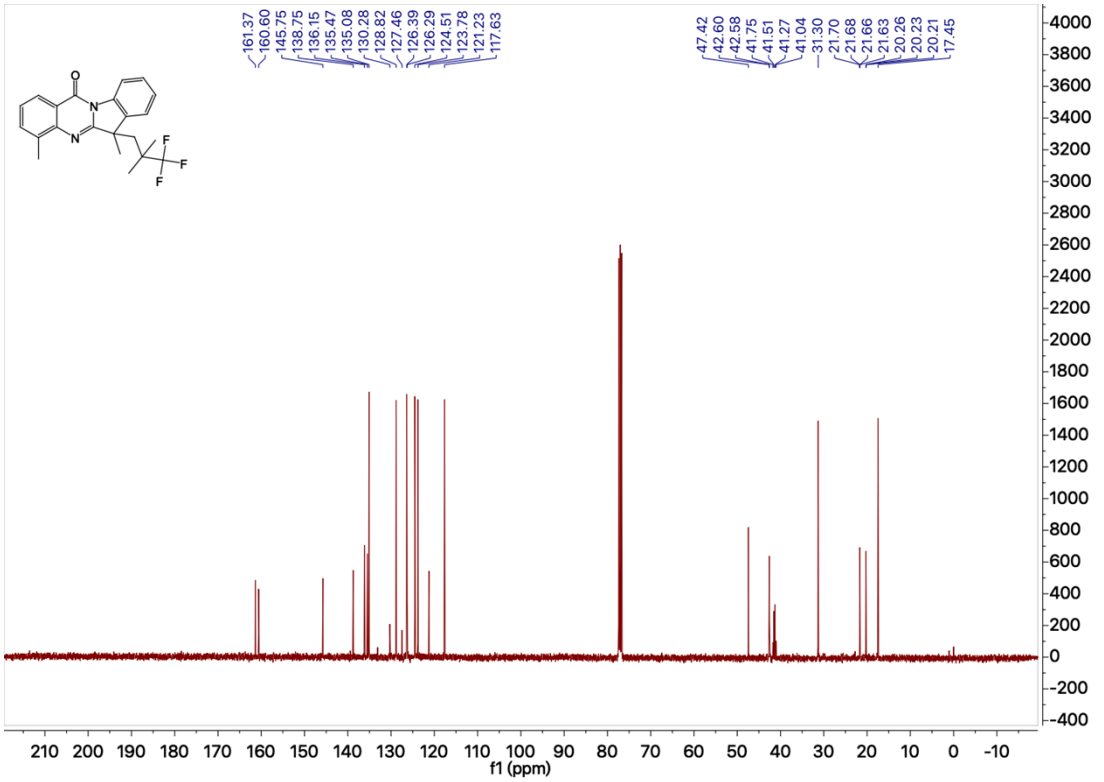

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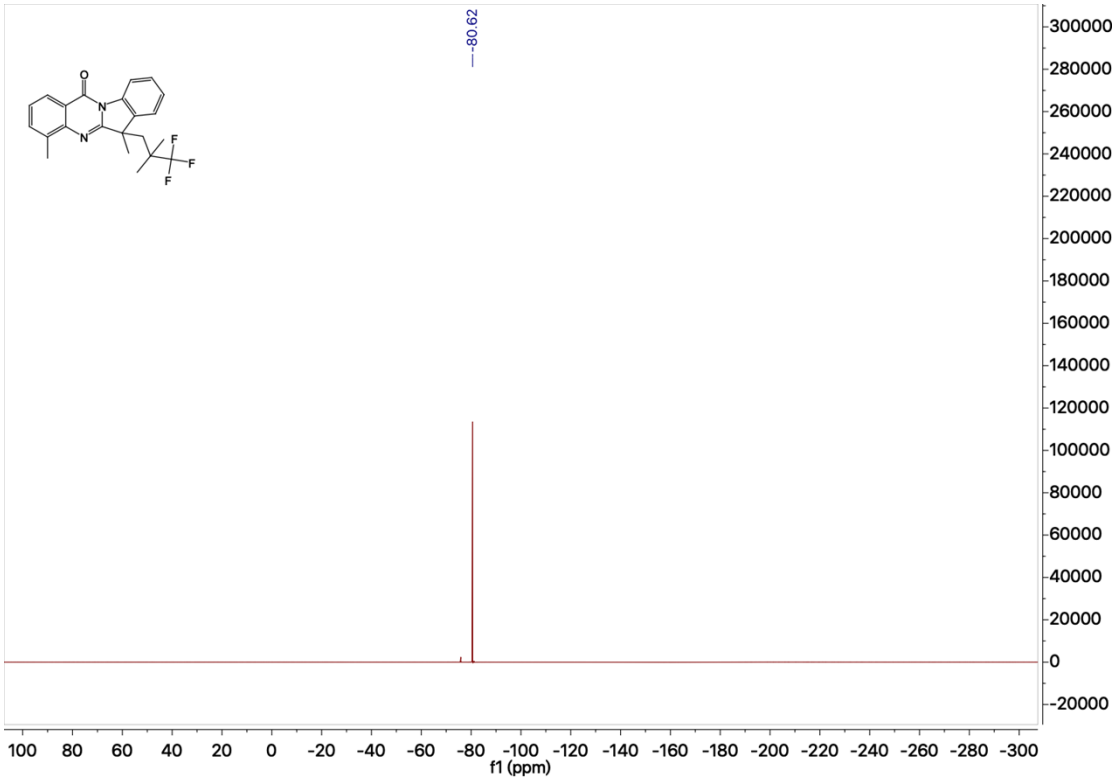

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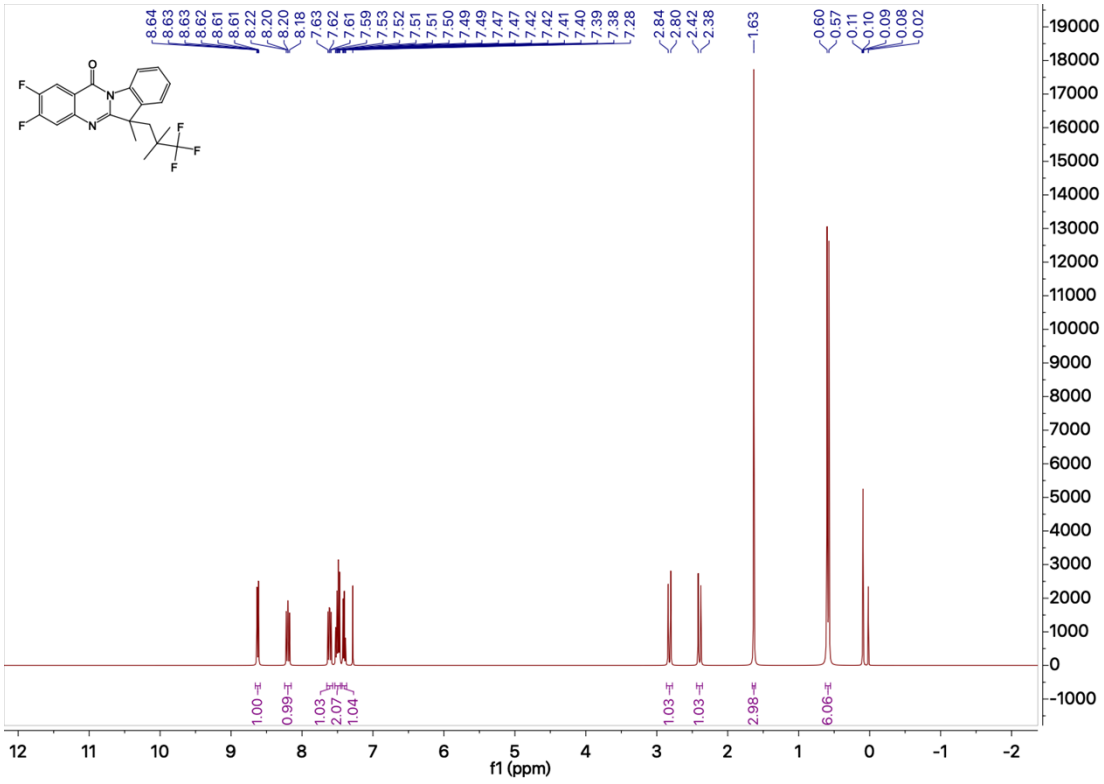

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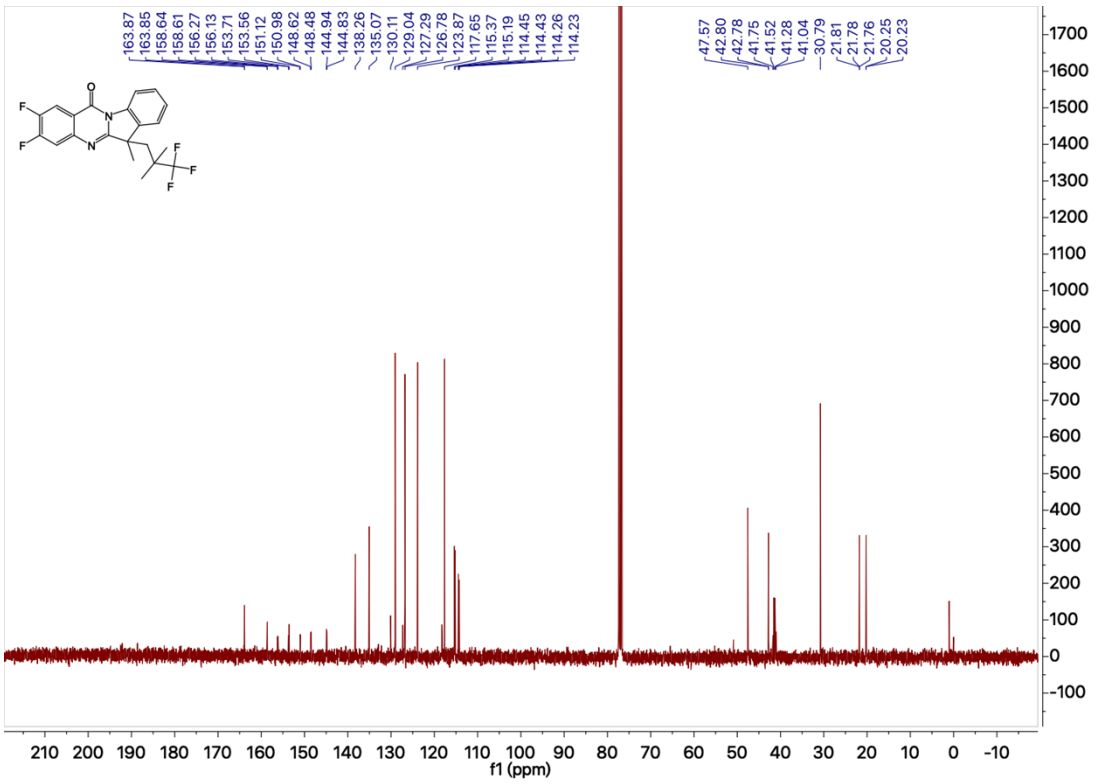

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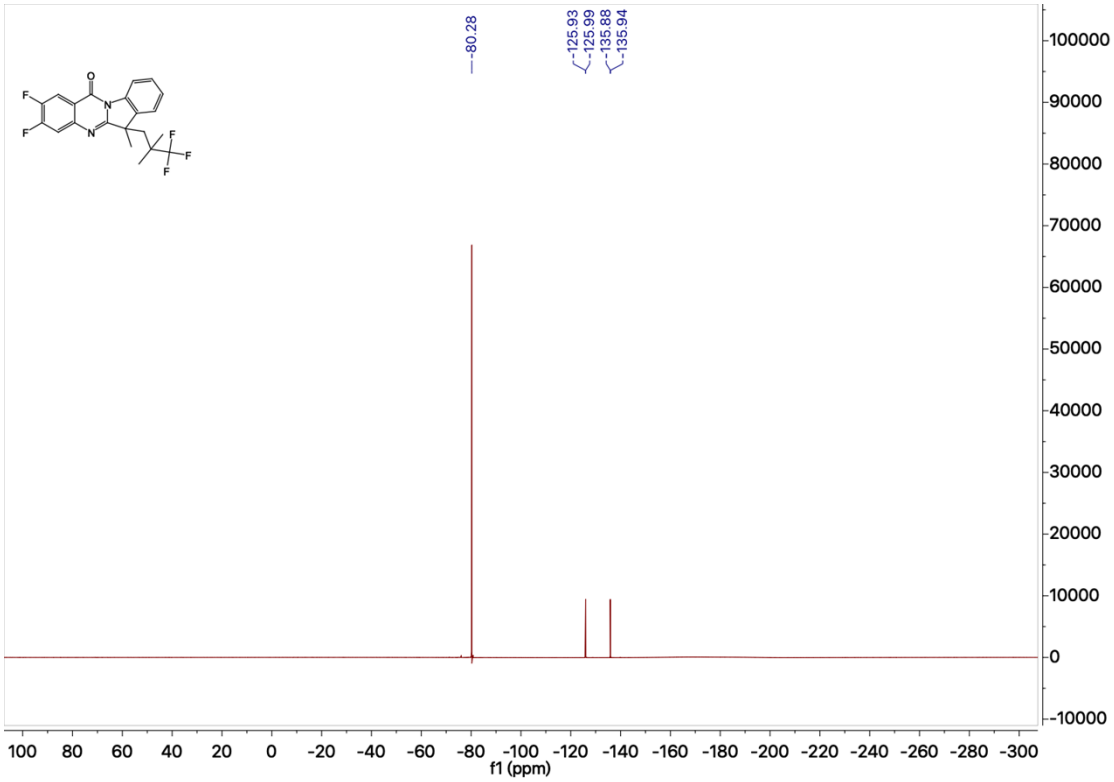

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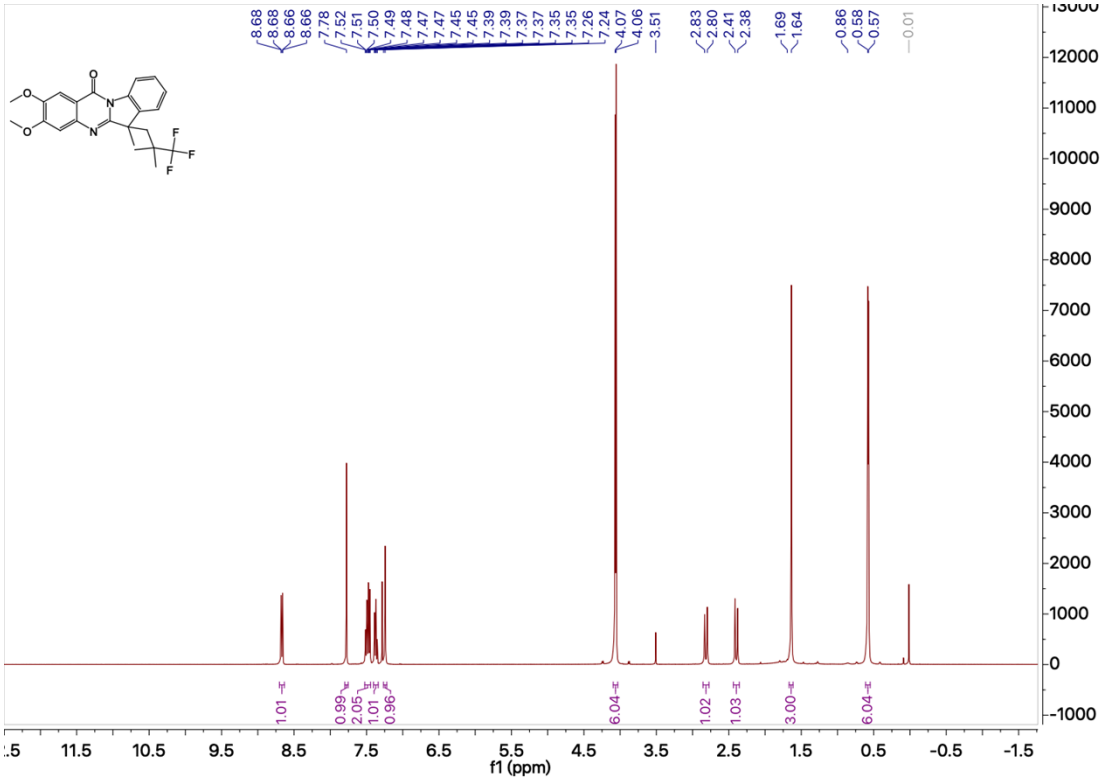

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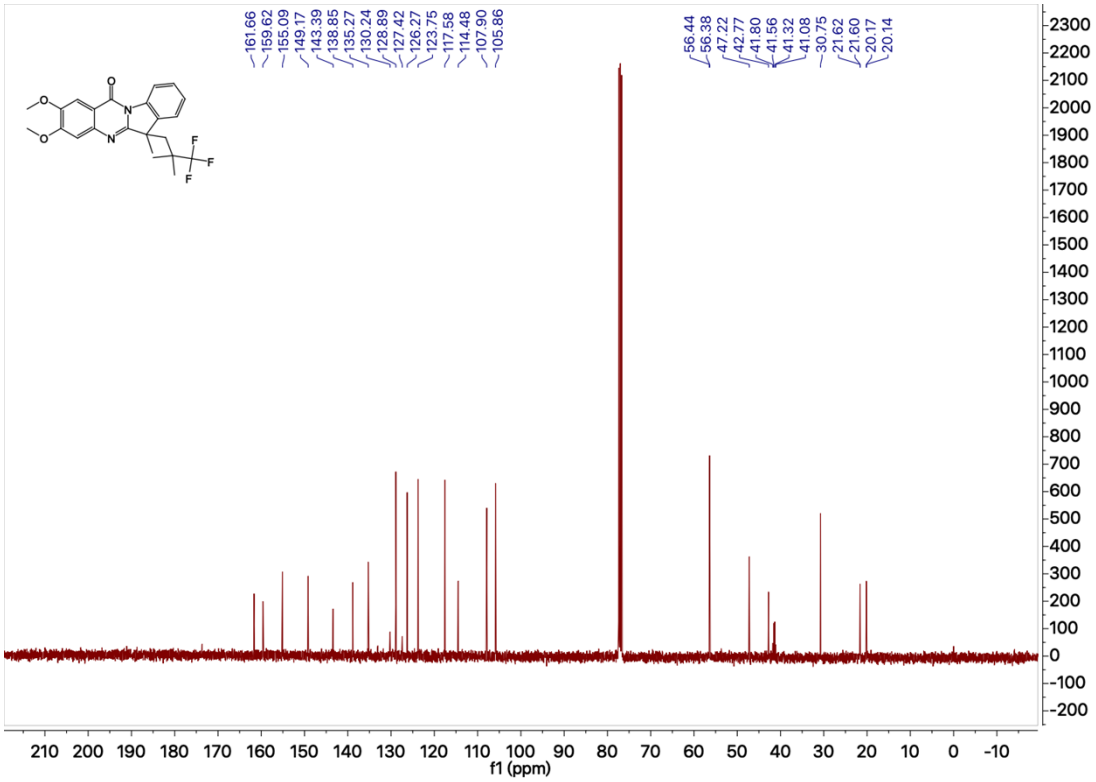

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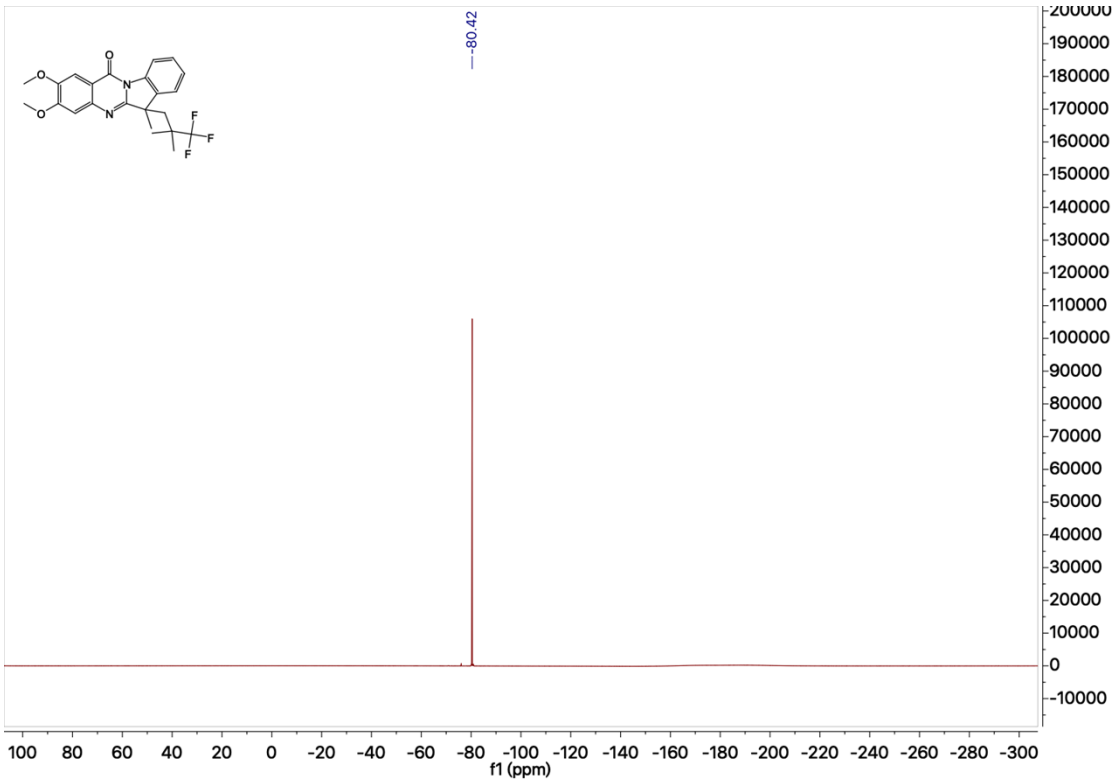

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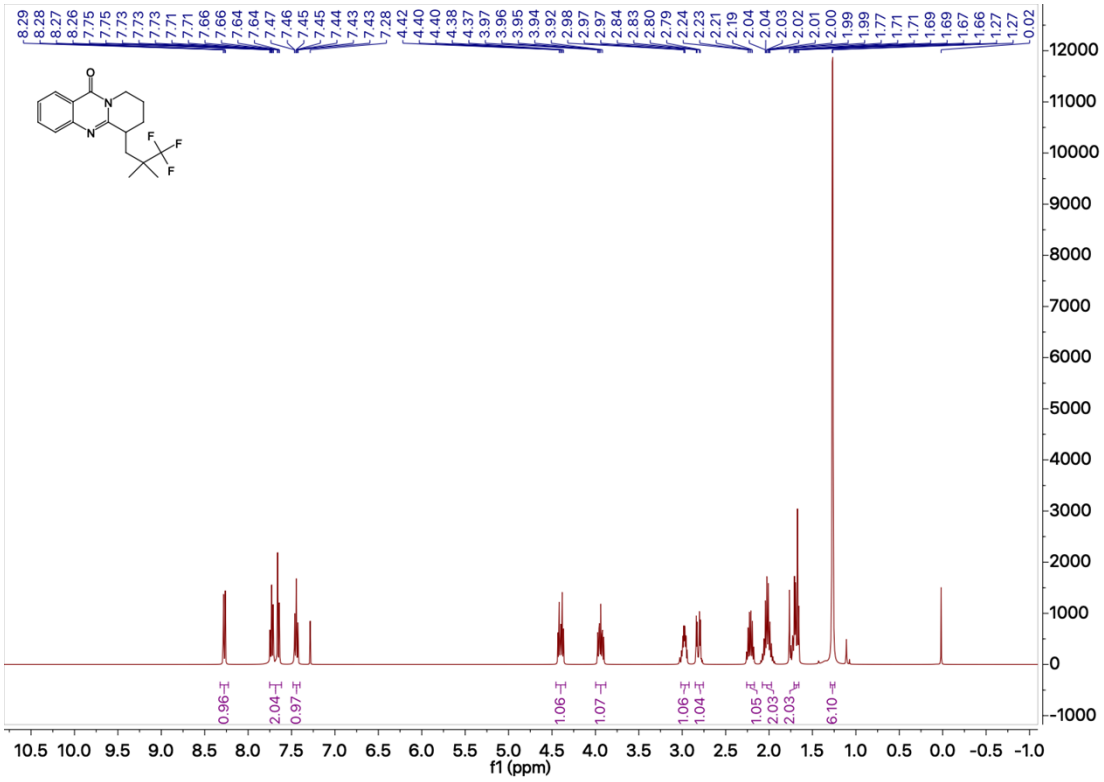
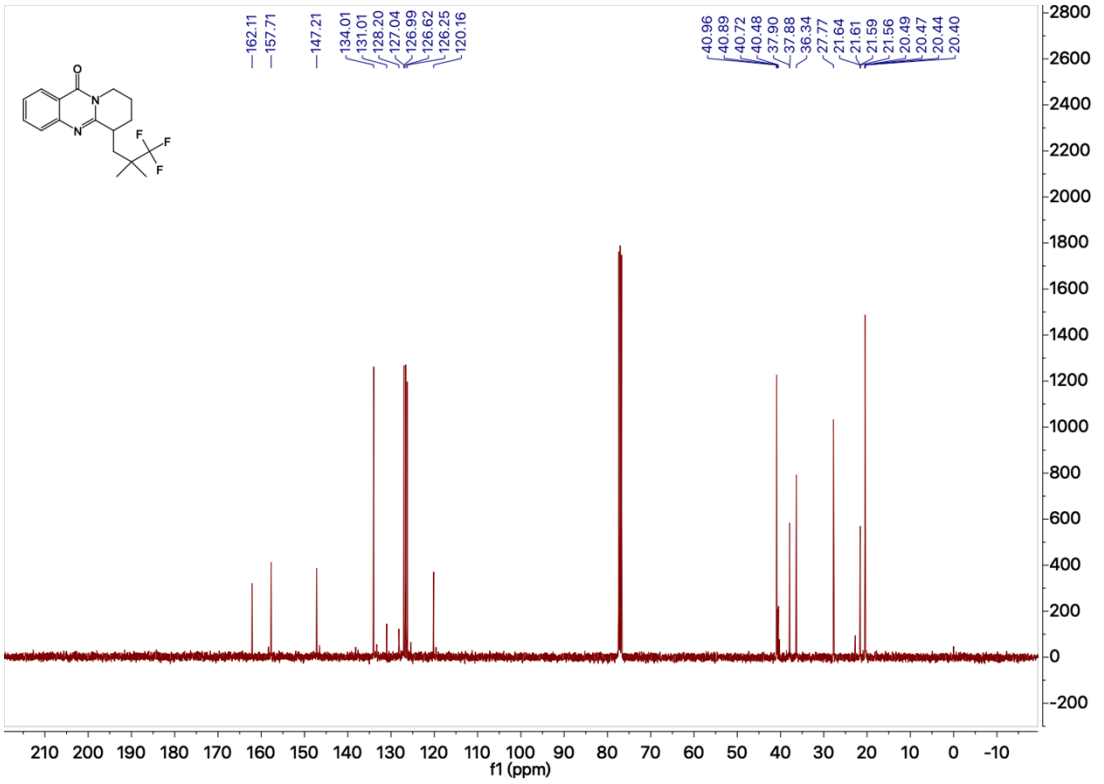
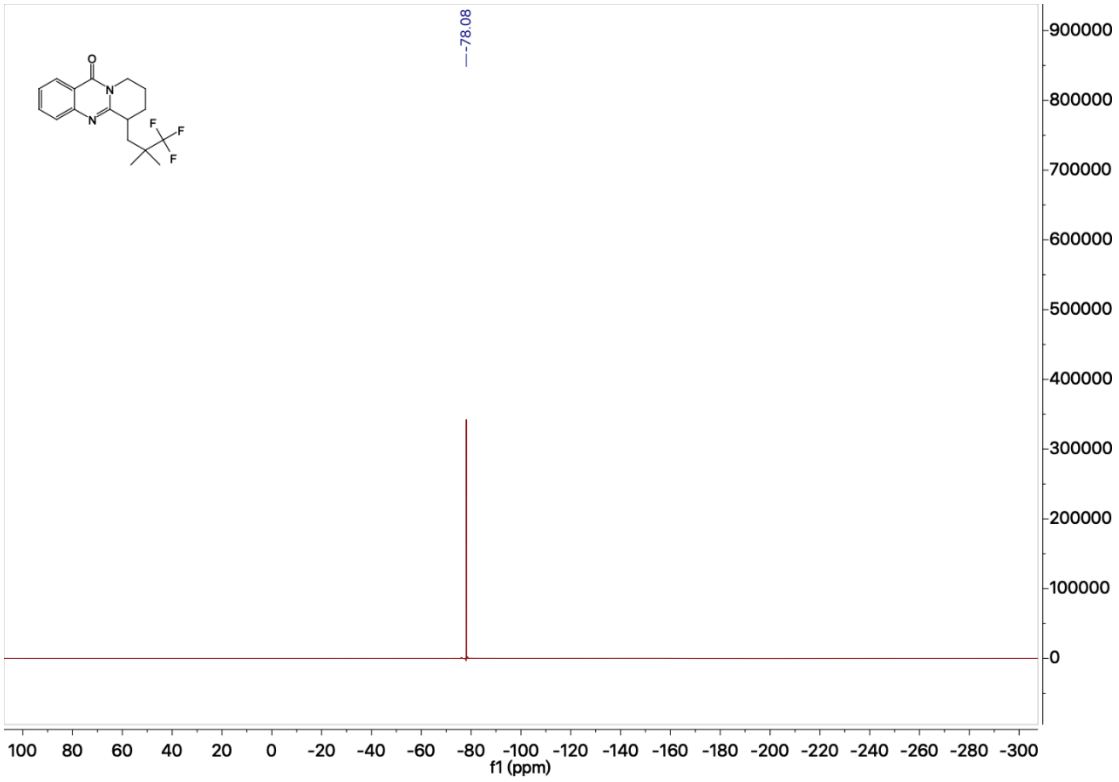


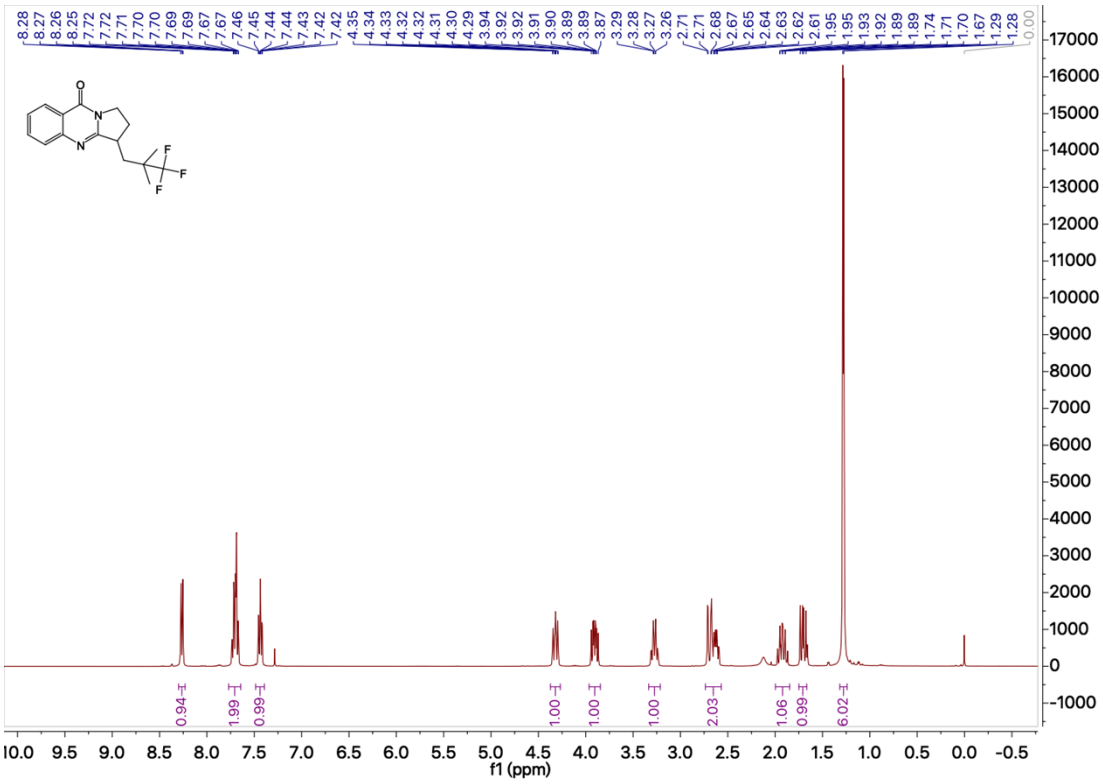
3an ^{13}C Chloroform-*d*, 101 MHz



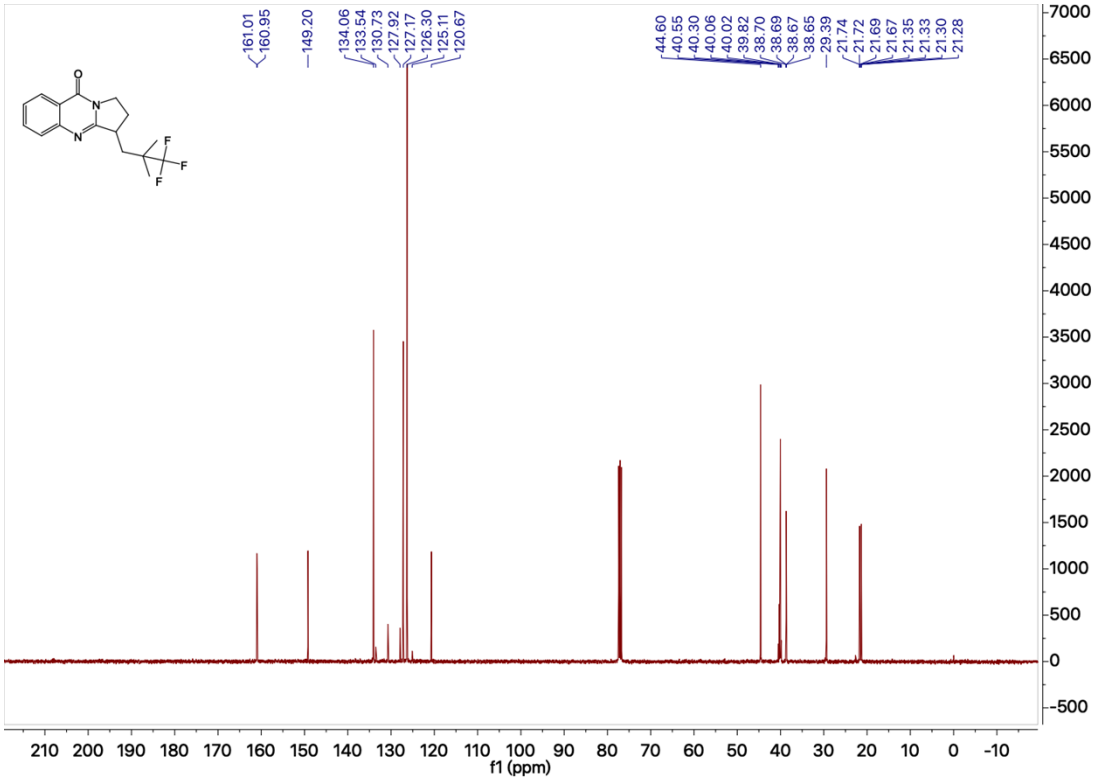
3an ^{19}F Chloroform-*d*, 376 MHz



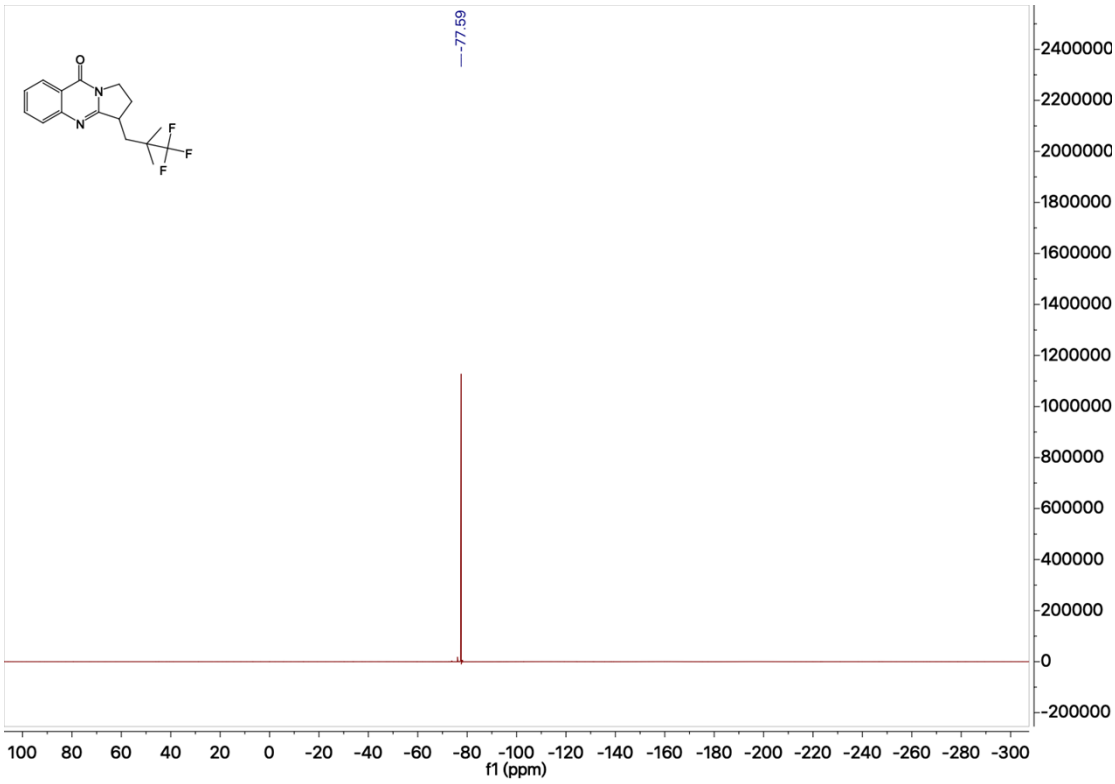
3ar ^{1}H Chloroform-*d*, 400 MHz



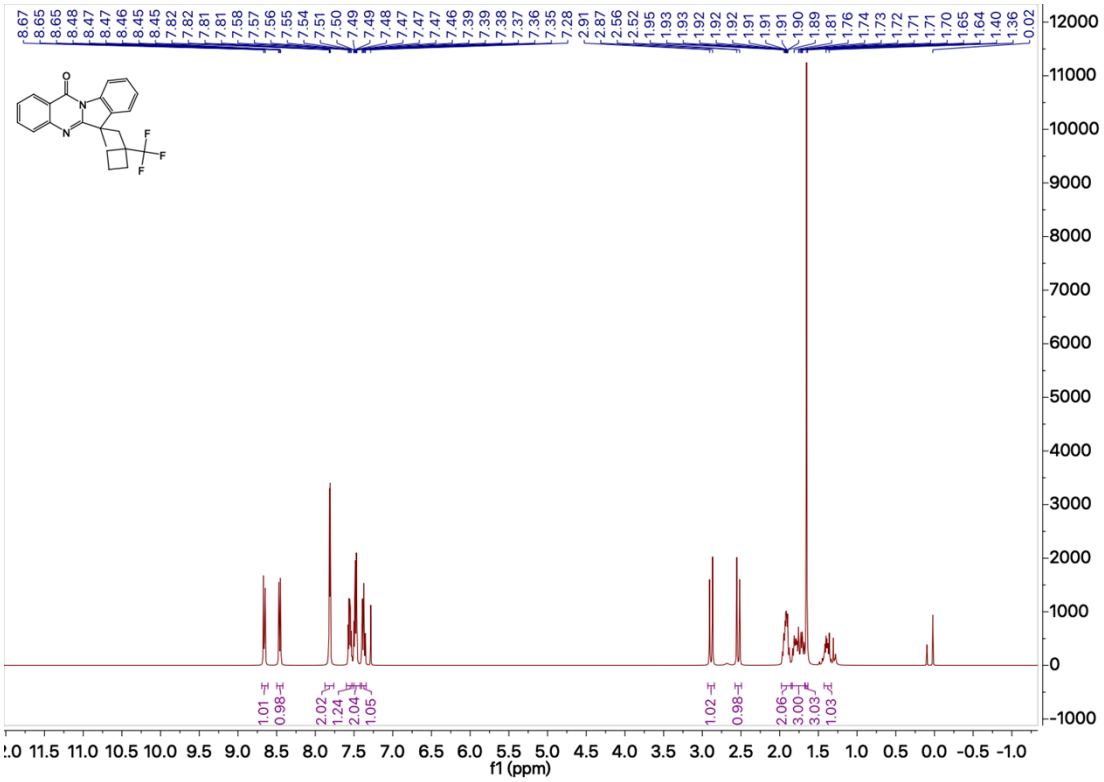
3ar ^{13}C Chloroform-*d*, 101 MHz



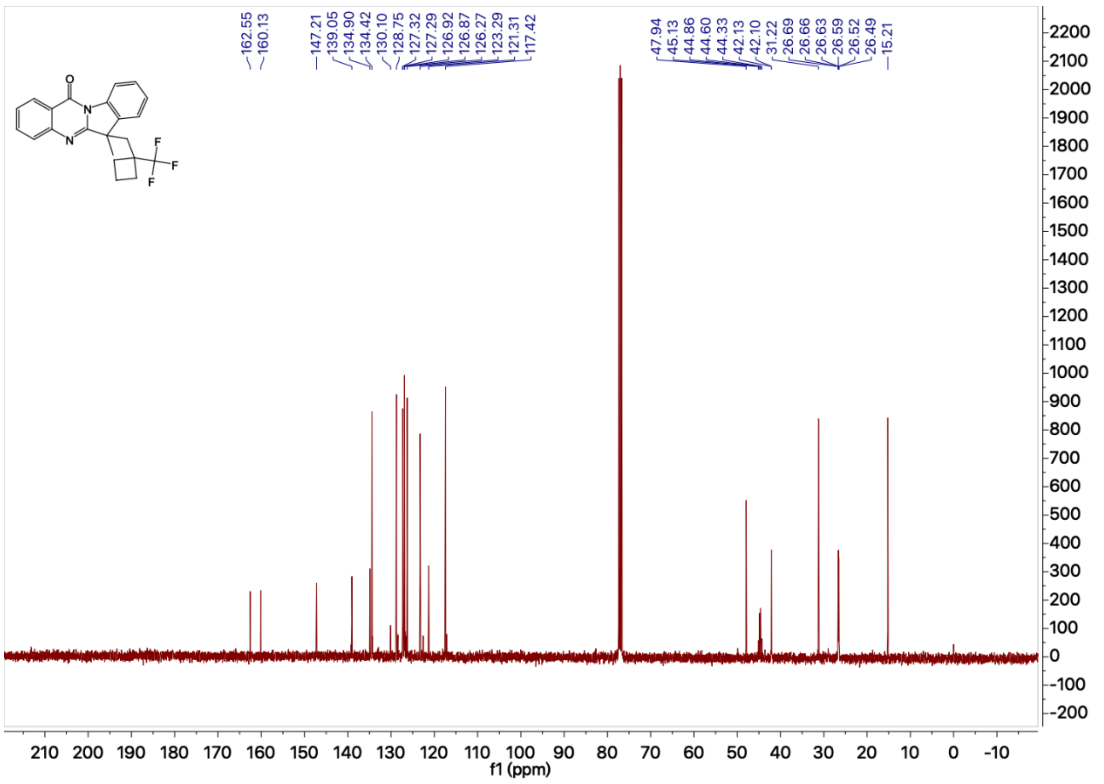
3ar ^{19}F Chloroform-*d*, 376 MHz



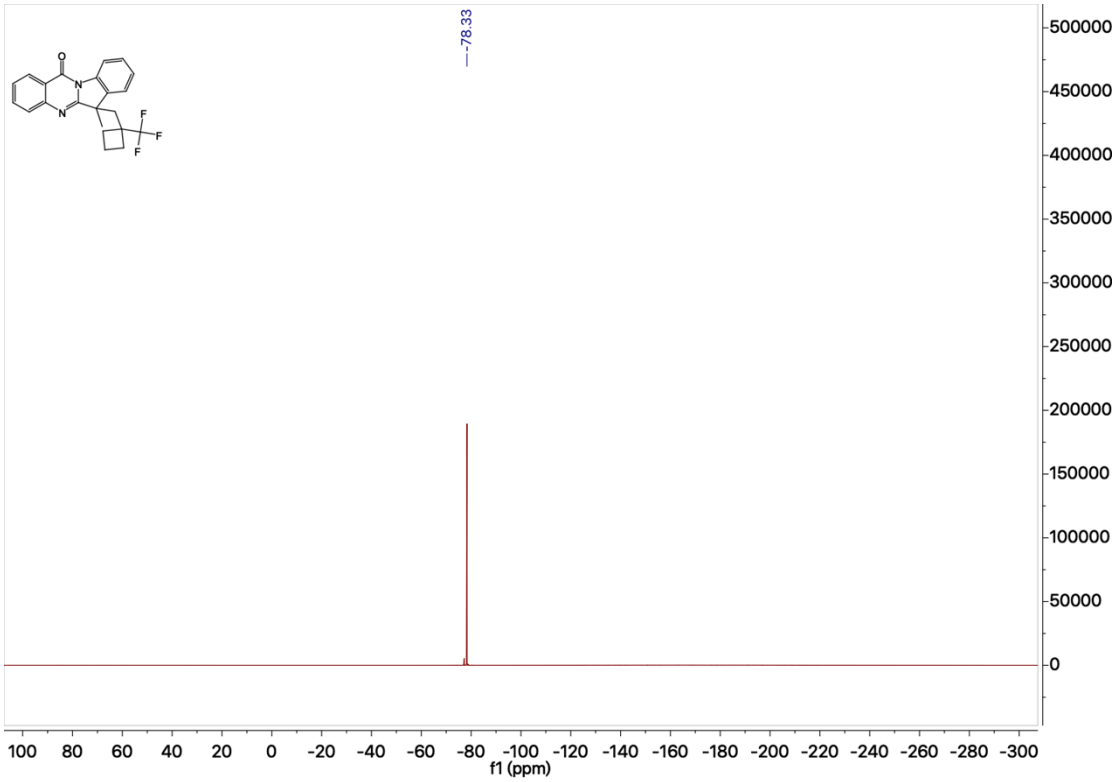
3ba ^{1}H Chloroform-*d*, 400 MHz



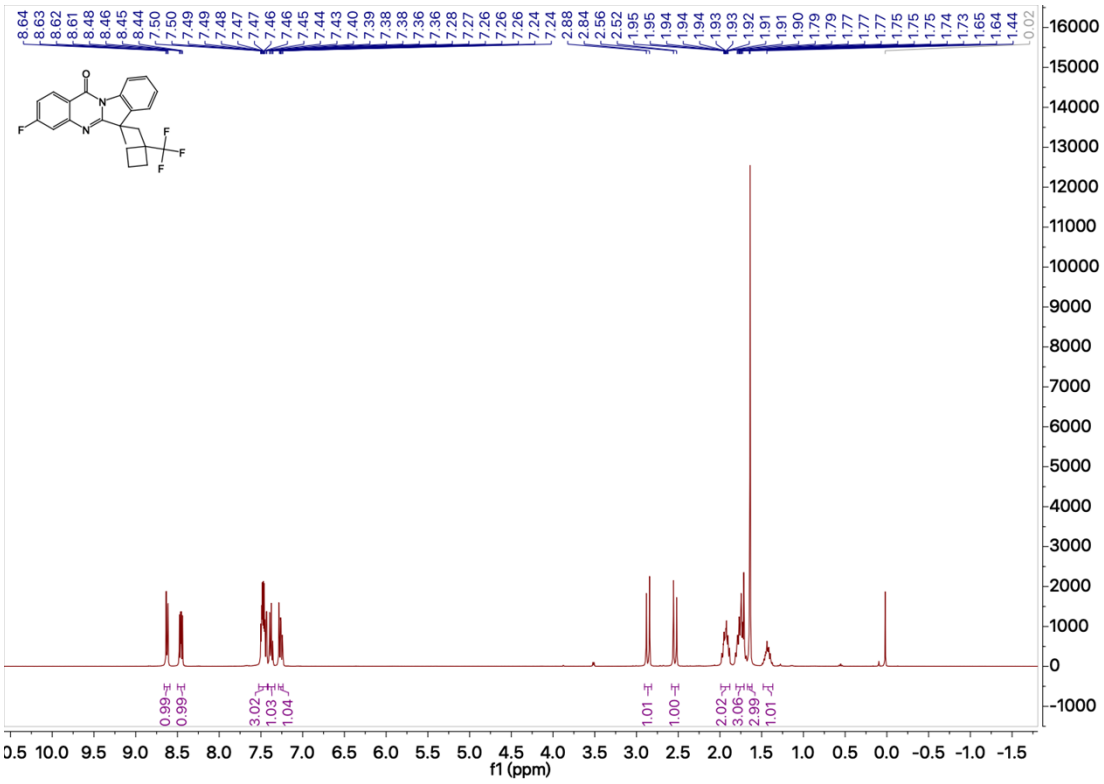
3ba ^{13}C Chloroform-*d*, 101 MHz



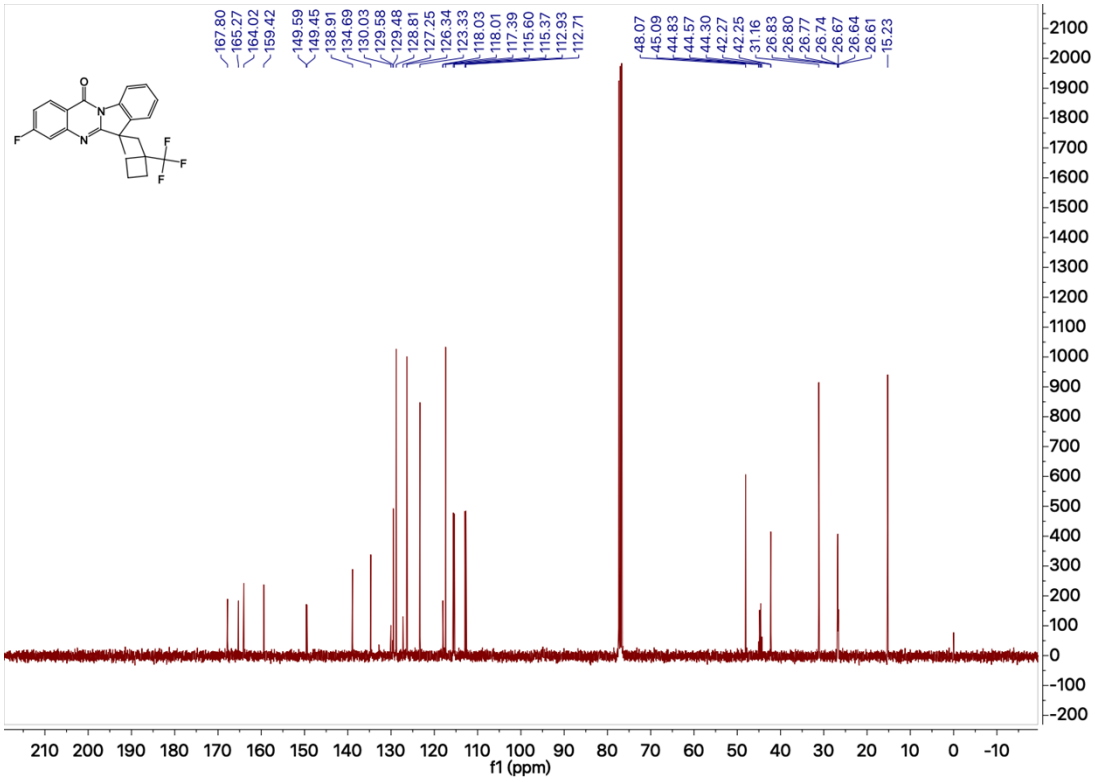
3ba ^{19}F Chloroform-*d*, 376 MHz



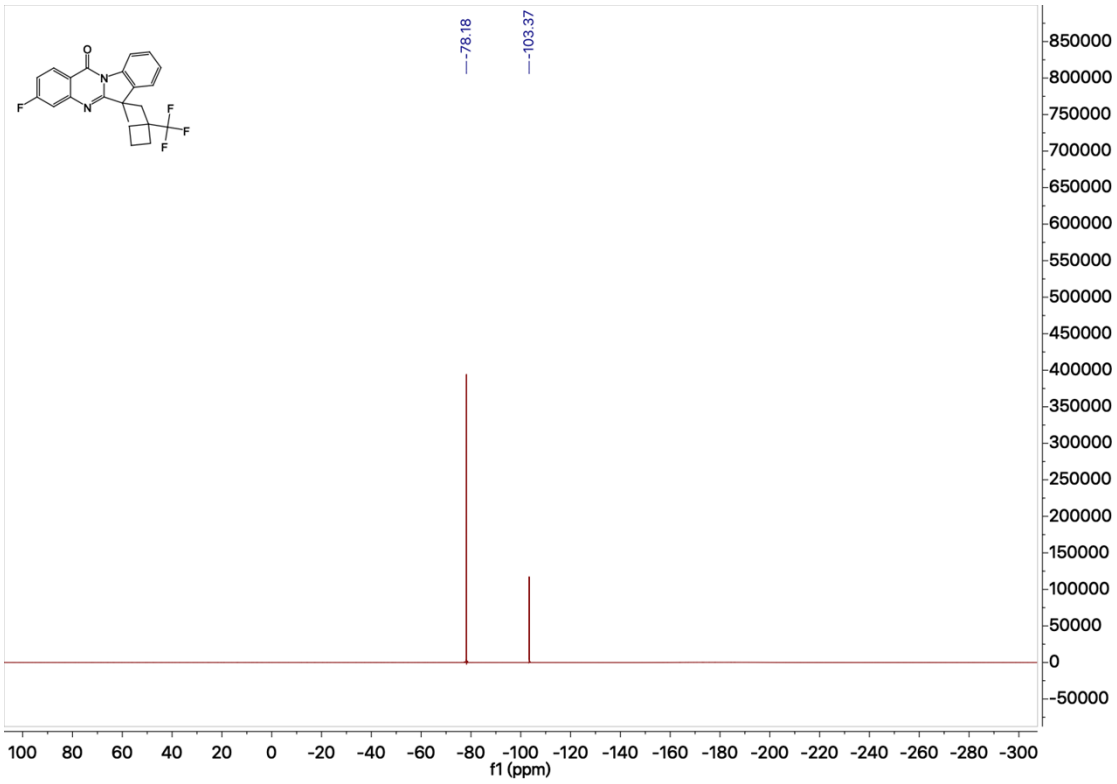
3ca ^{1}H Chloroform-*d*, 400 MHz



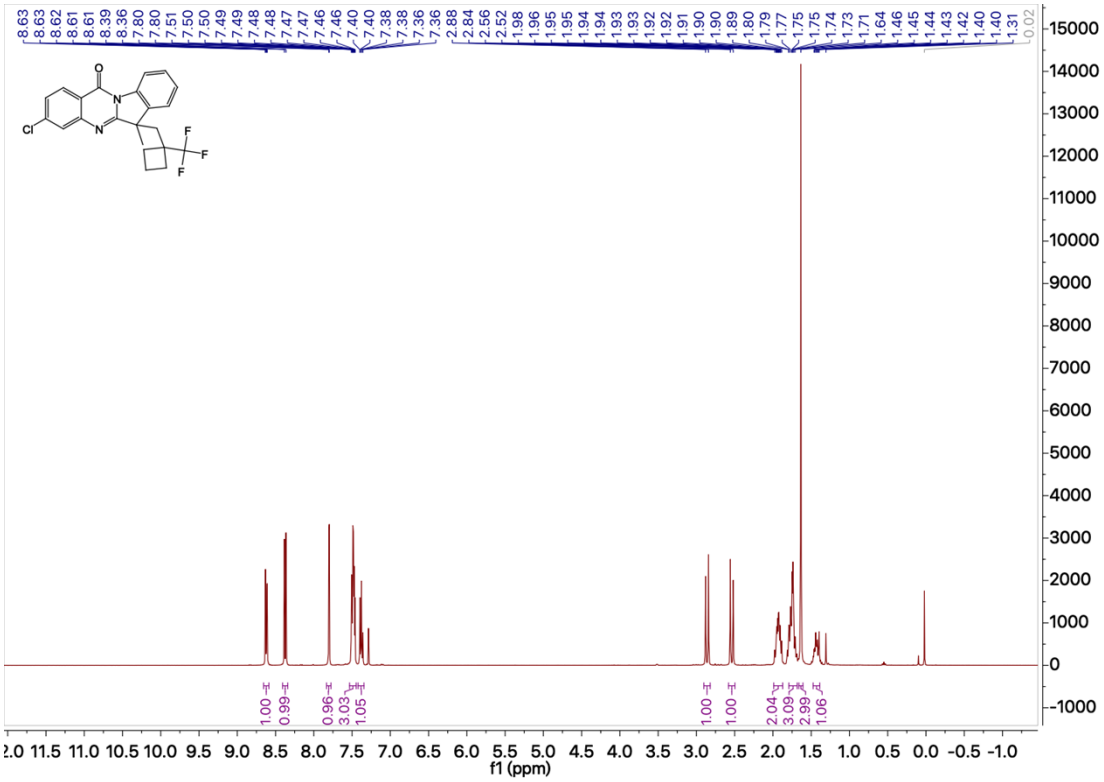
3ca ^{13}C Chloroform-*d*, 101 MHz



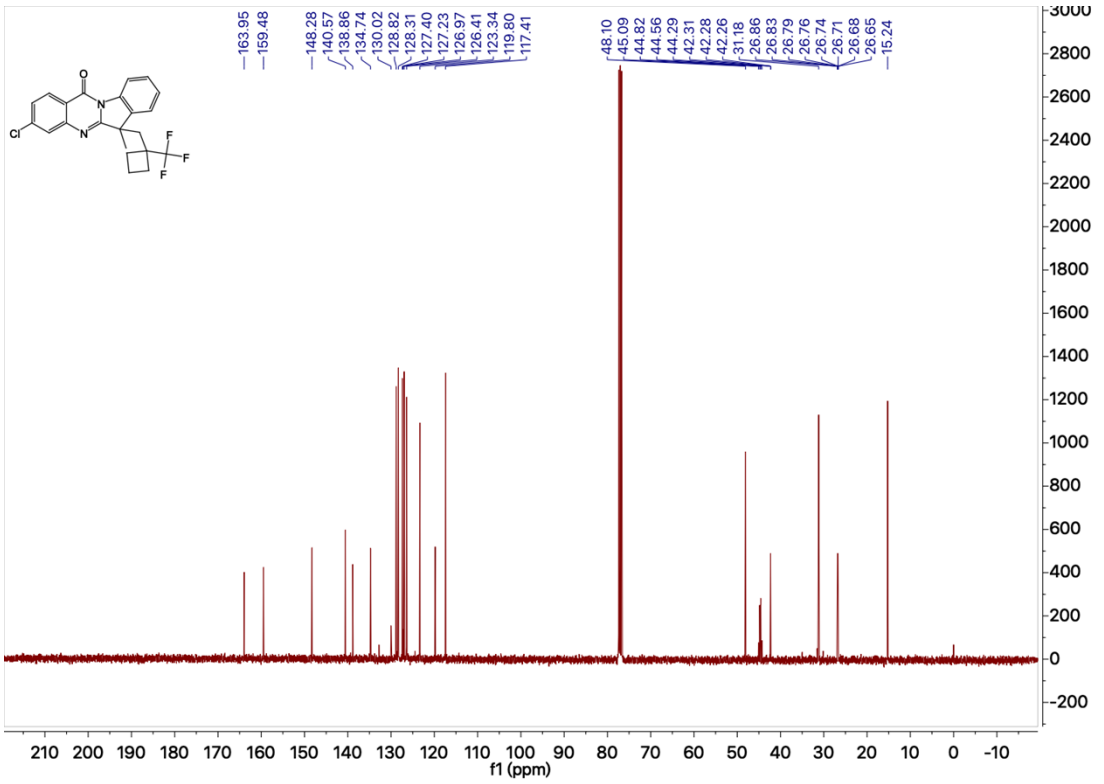
3ca ^{19}F Chloroform-*d*, 376 MHz



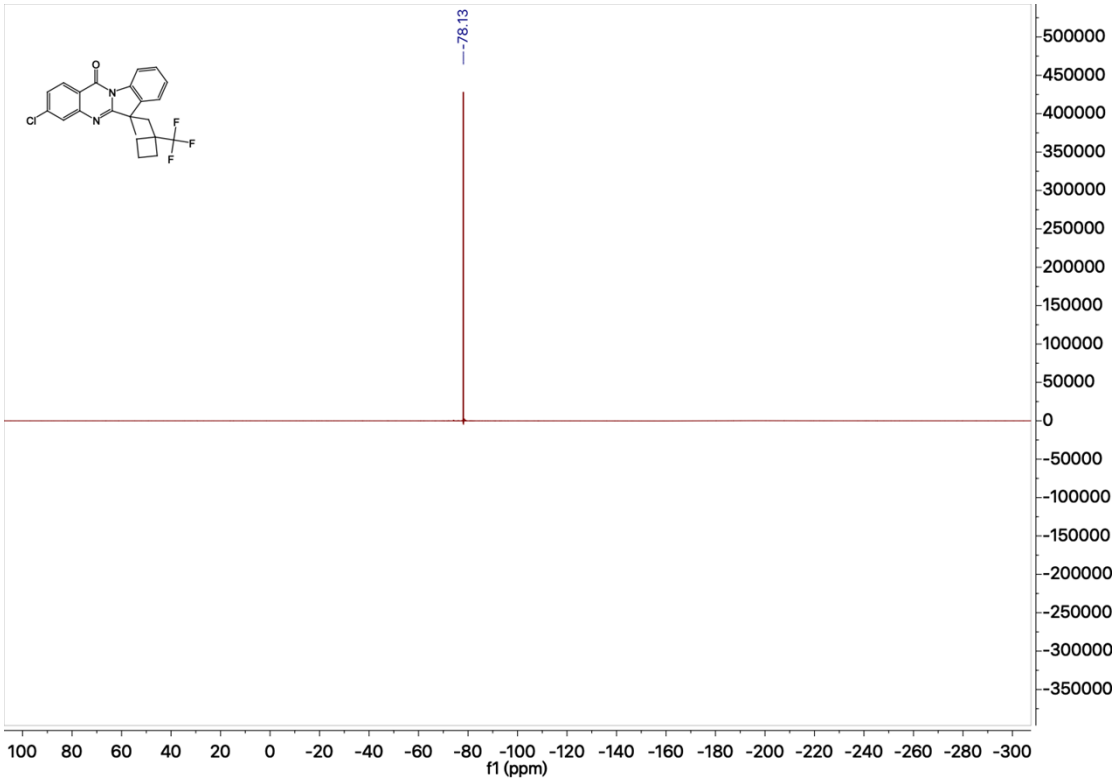
3da ^{1}H Chloroform-*d*, 400 MHz



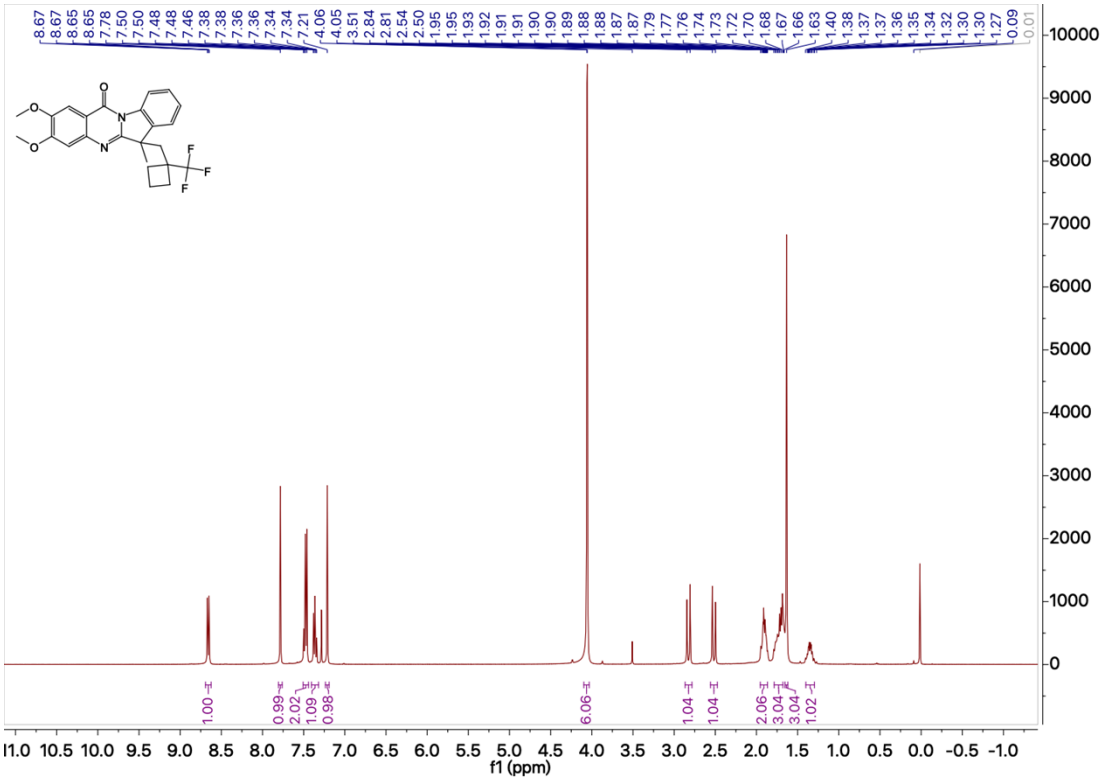
3da ^{13}C Chloroform-*d*, 101 MHz



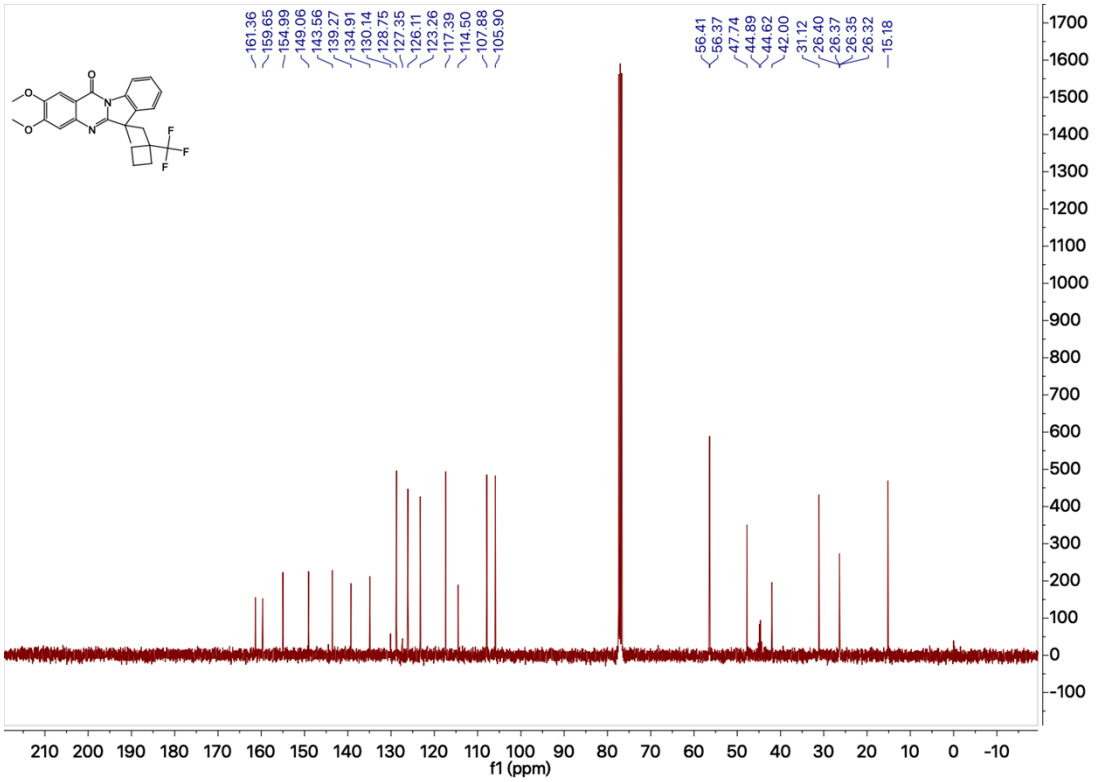
3da ^{19}F Chloroform-*d*, 376 MHz



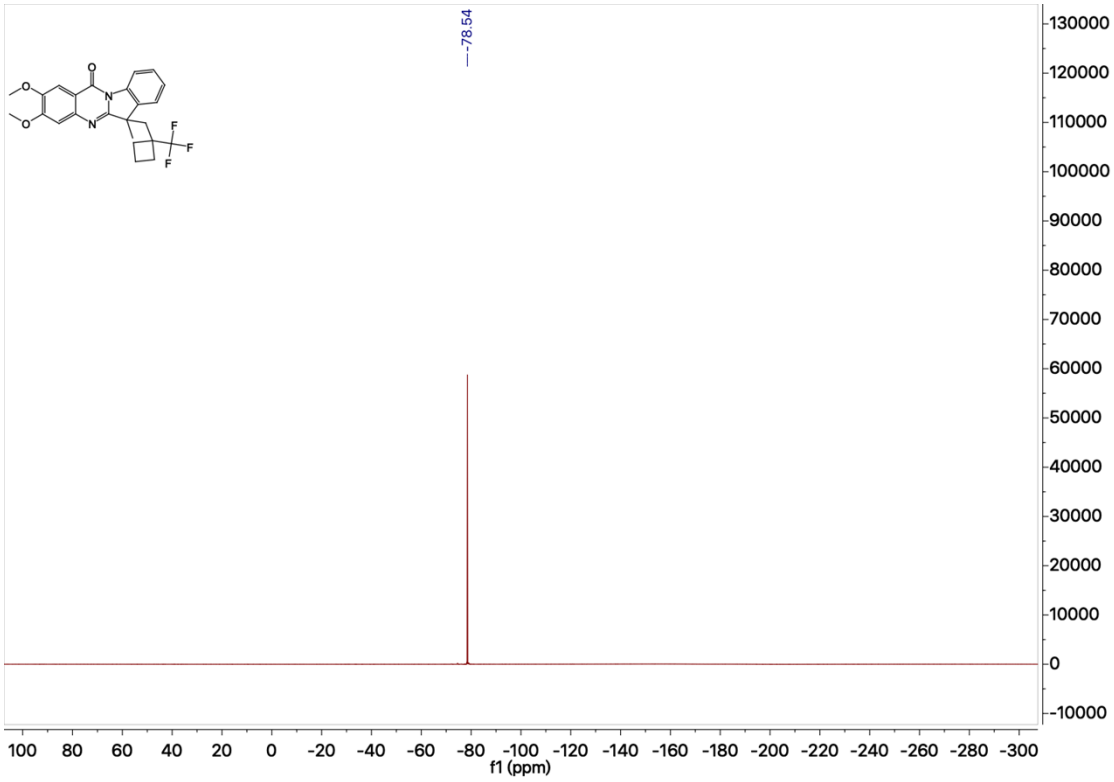
3ea ^{1}H Chloroform-*d*, 400 MHz



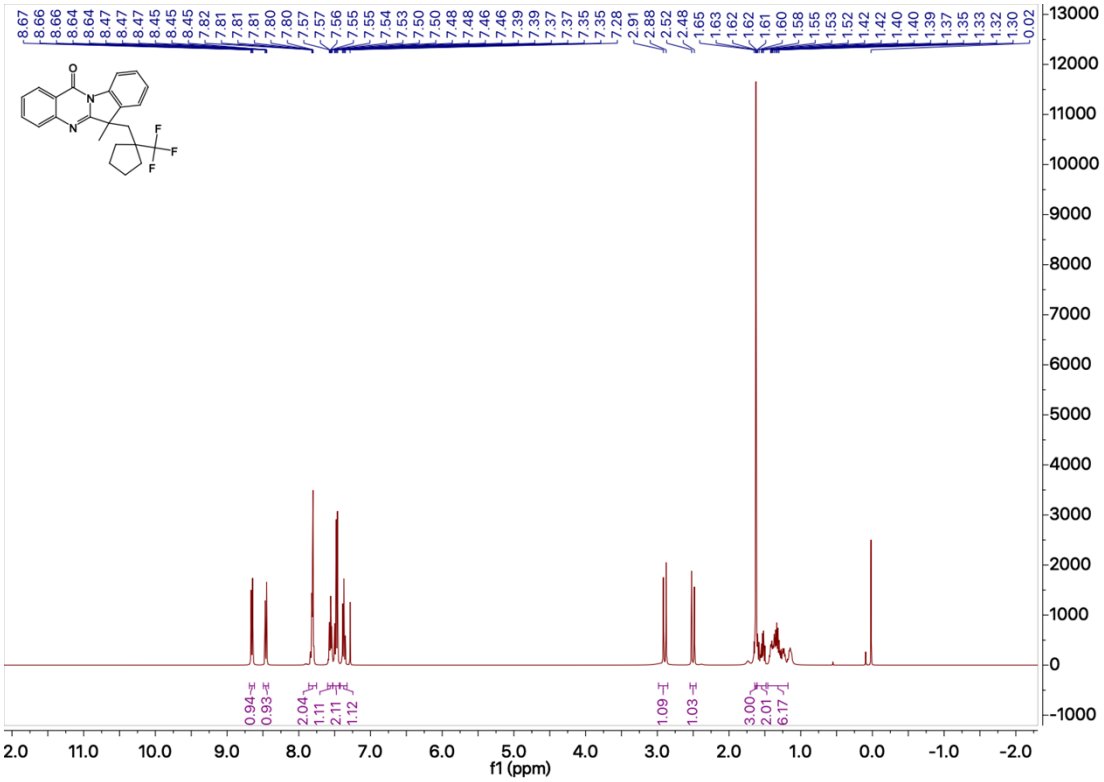
3ea ^{13}C Chloroform-*d*, 101 MHz



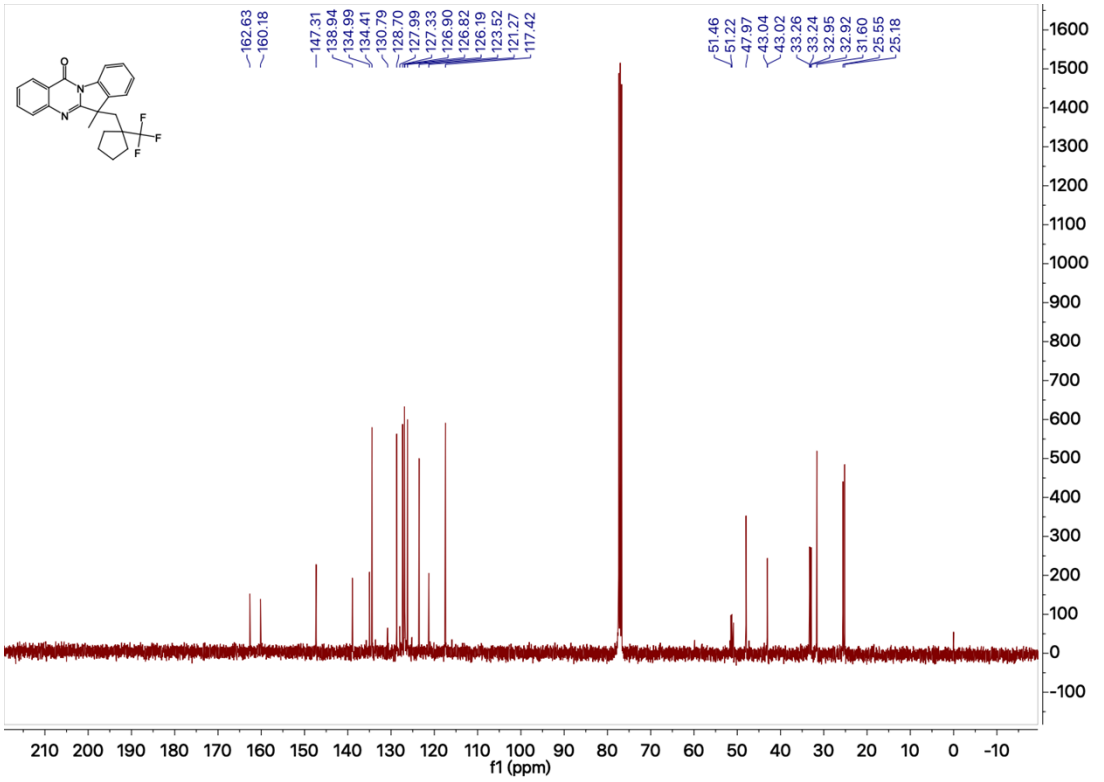
3ea ^{19}F Chloroform-*d*, 376 MHz



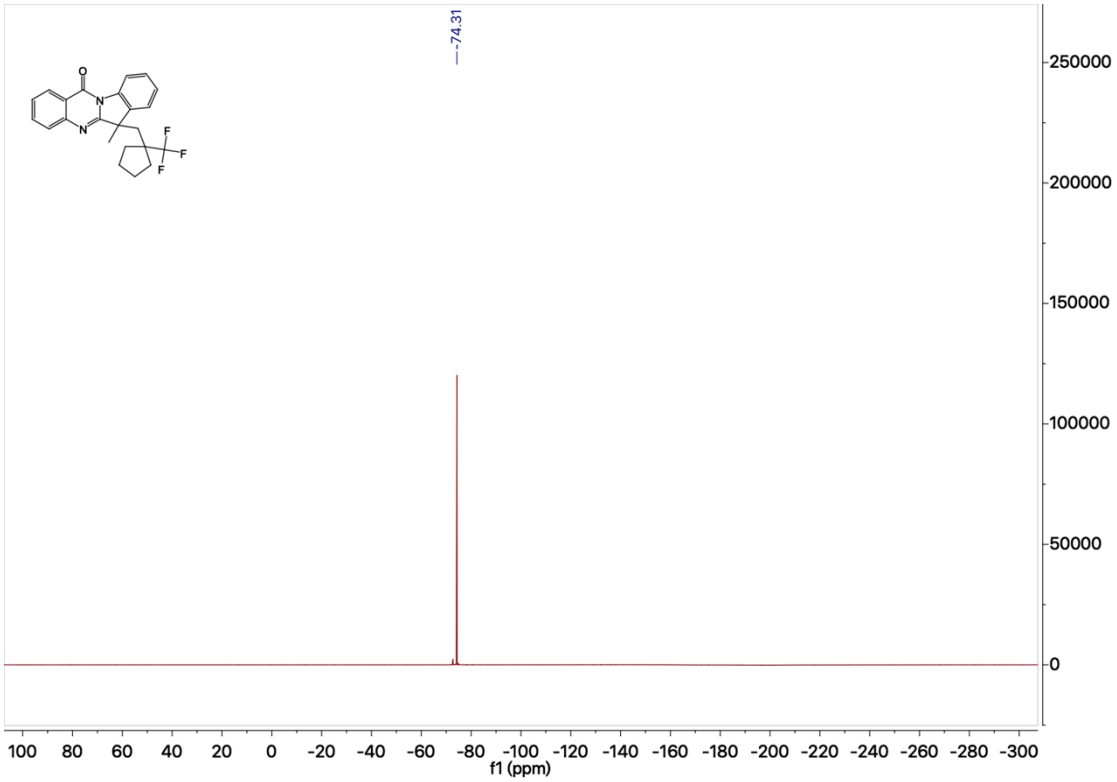
3fa ^{1}H Chloroform-*d*, 400 MHz



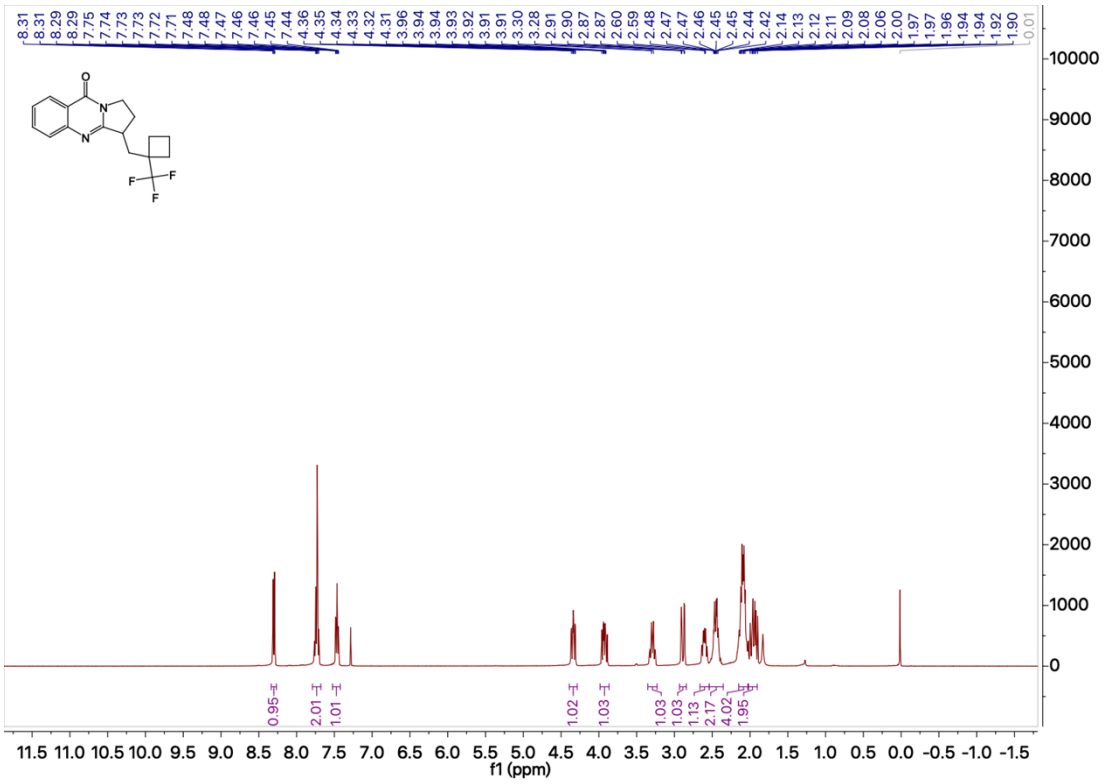
3fa ^{13}C Chloroform-*d*, 101 MHz



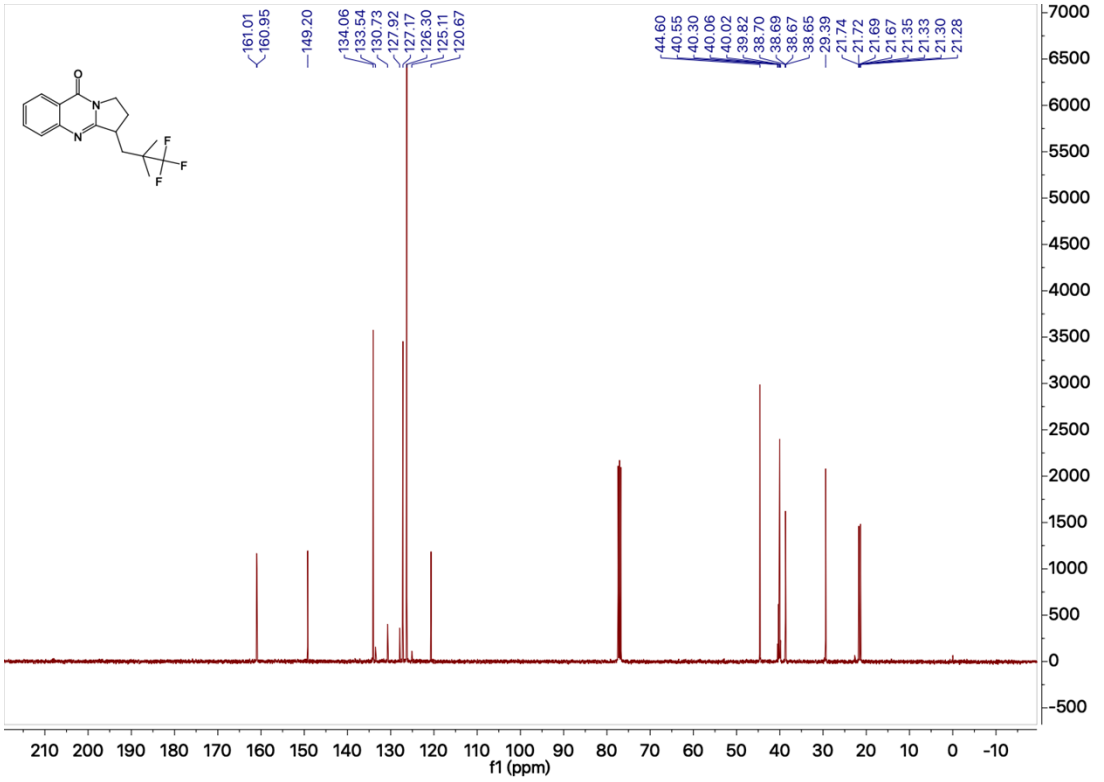
3fa ^{19}F Chloroform-*d*, 376 MHz



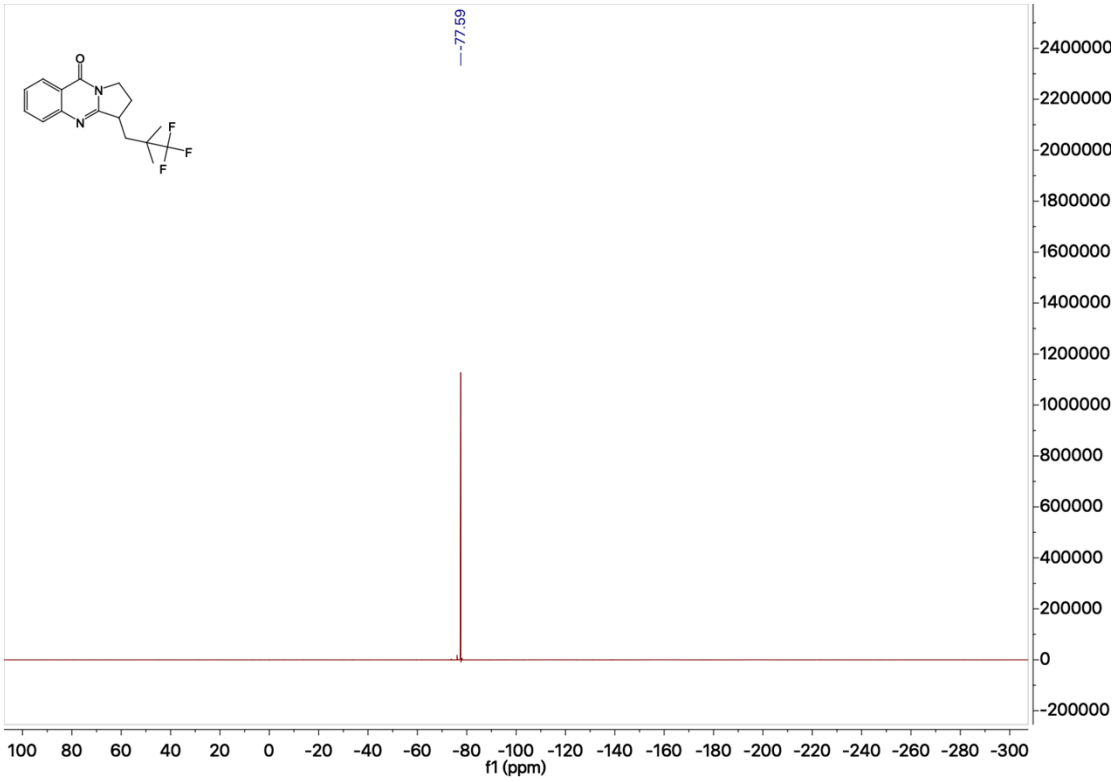
3ga ^{1}H Chloroform-*d*, 400 MHz



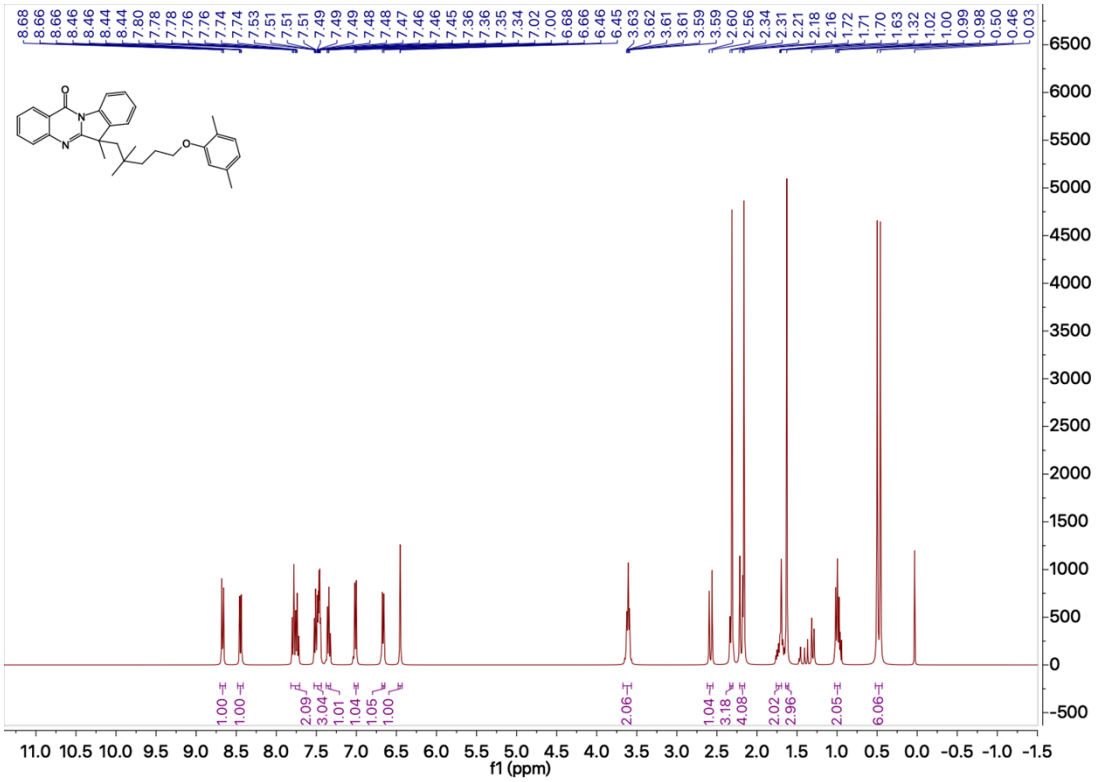
3ga ^{13}C Chloroform-*d*, 101 MHz



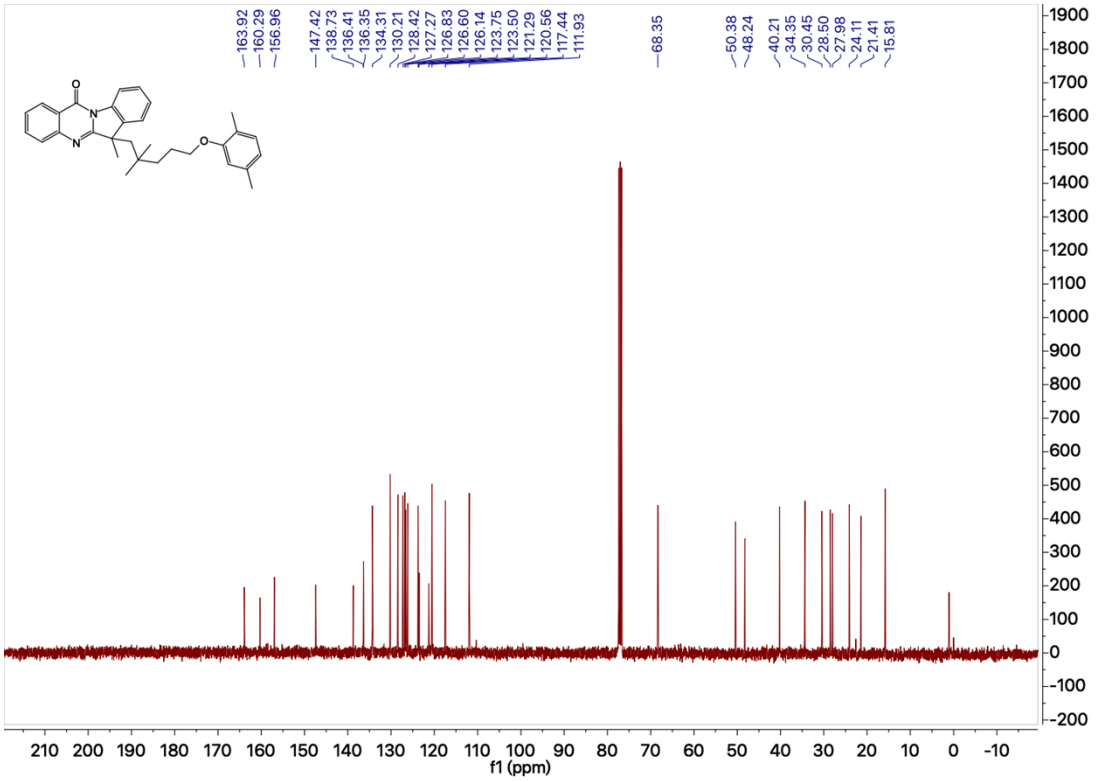
3ga ^{19}F Chloroform-*d*, 376 MHz



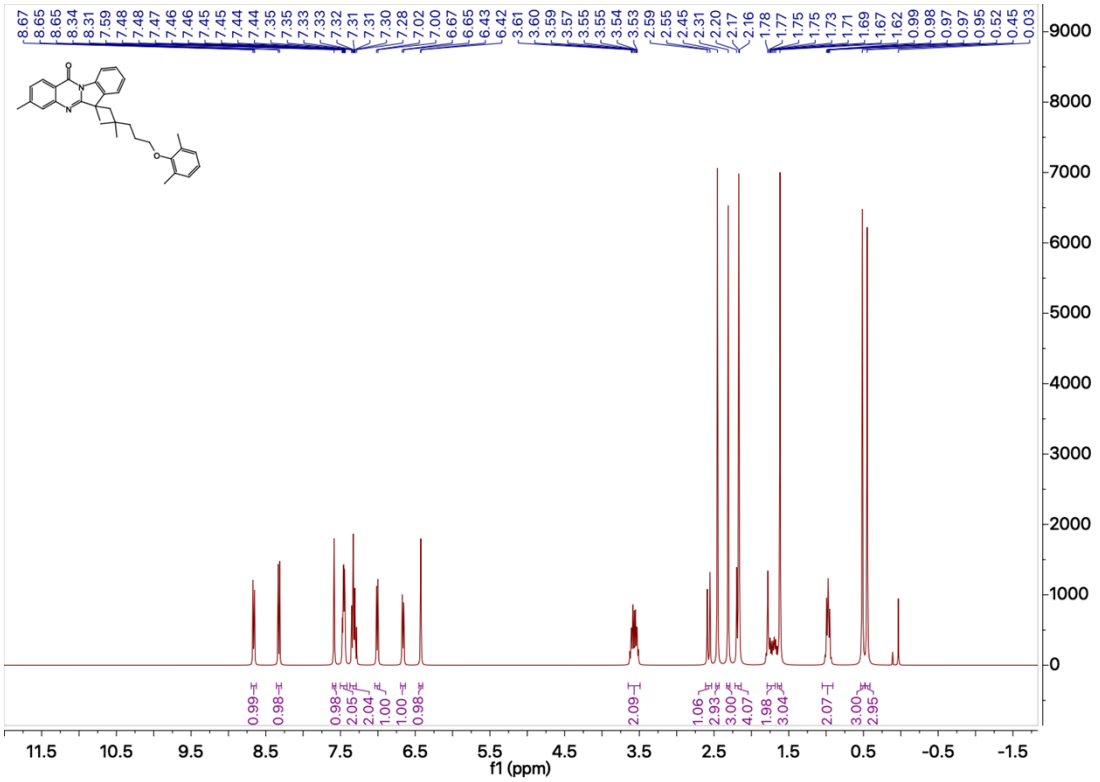
3ha ^{1}H Chloroform-*d*, 400 MHz



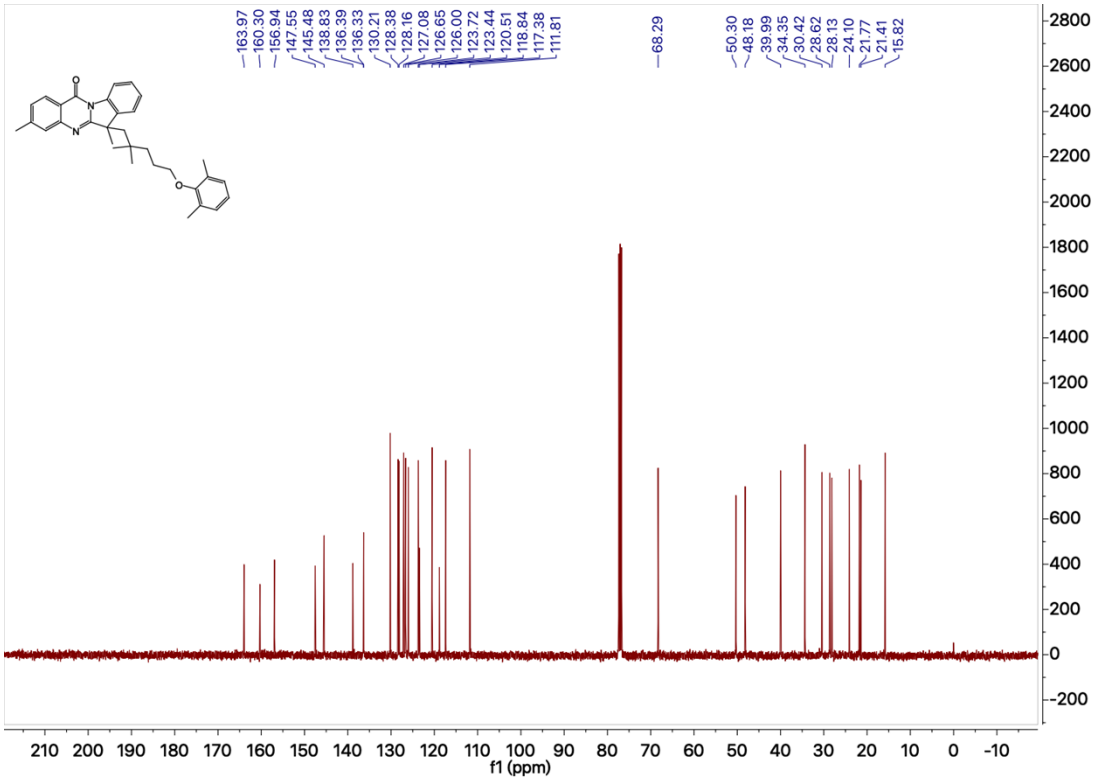
3ha ^{13}C Chloroform-*d*, 101 MHz



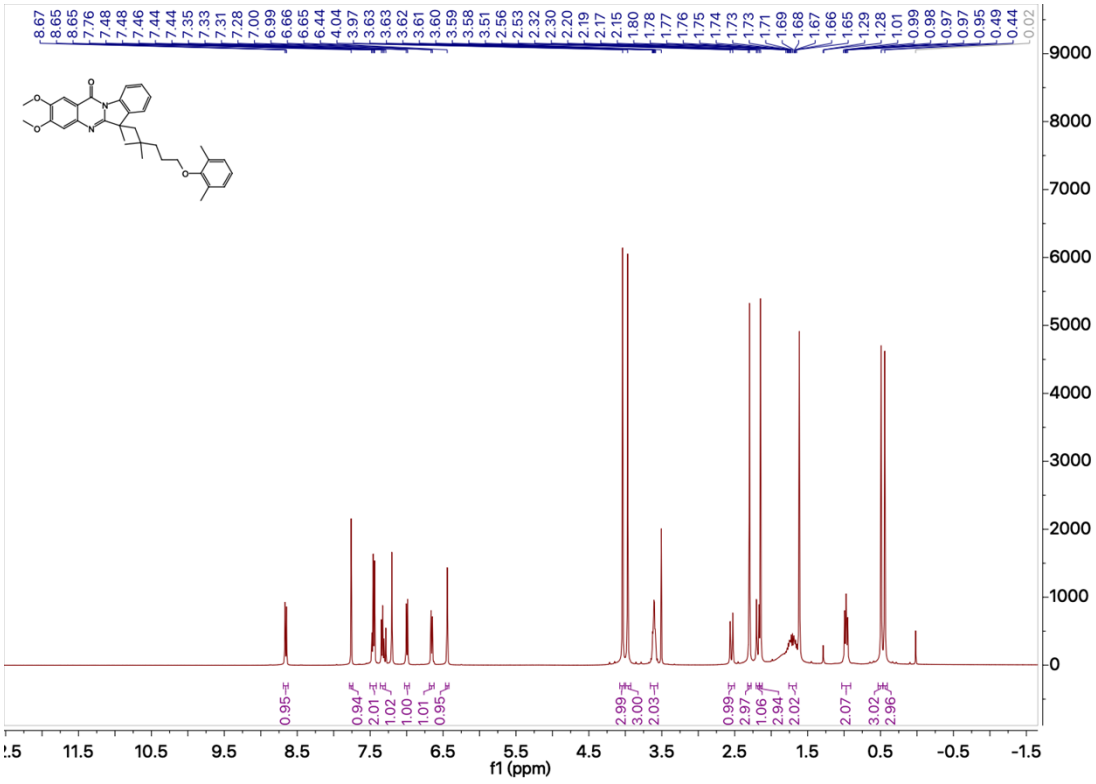
3ia ^{1}H Chloroform-*d*, 400 MHz



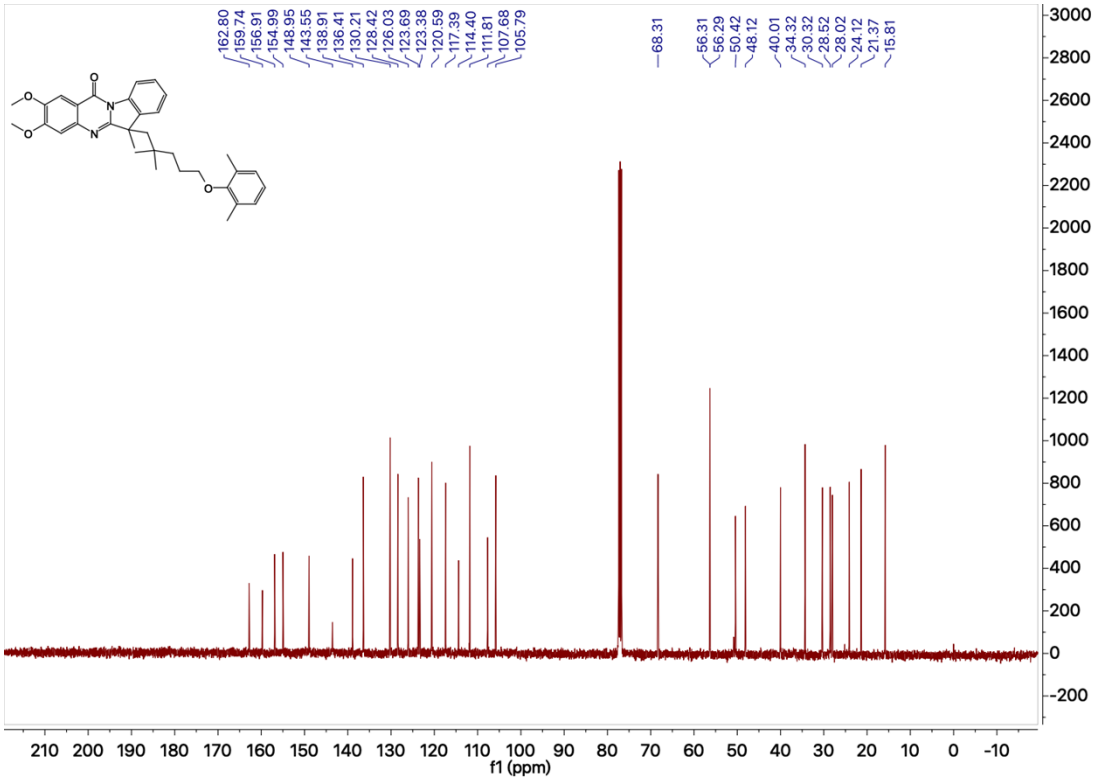
3ia ^{13}C Chloroform-*d*, 101 MHz



3ja ^{1}H Chloroform-*d*, 400 MHz



3ja ^{13}C Chloroform-*d*, 101 MHz



V. Computational Details

All DFT theoretical calculations have been carried out using the Gaussian09 program package[1]. The B3LYP[2] density functional method with the D3(BJ) dispersion correction was employed in this work to carry out all the computations. The 6-31G(d) basis set was used for the atoms in geometry optimizations using the PCM model[3] with DMSO as the solvent. Vibrational frequency analyses at the same level of theory were performed on all optimized structures to characterize stationary points as local minima or transition states. Furthermore, intrinsic reaction coordinate (IRC) computations were carried out to confirm that transition states connect to the appropriate reactants and products. The single-point energy calculations were carried out using the 6-311++g(d,p) basis set to provide better energy correction.

(1) Calculated IRC Pathways and Imaginary Frequencies Vector of all Transition States

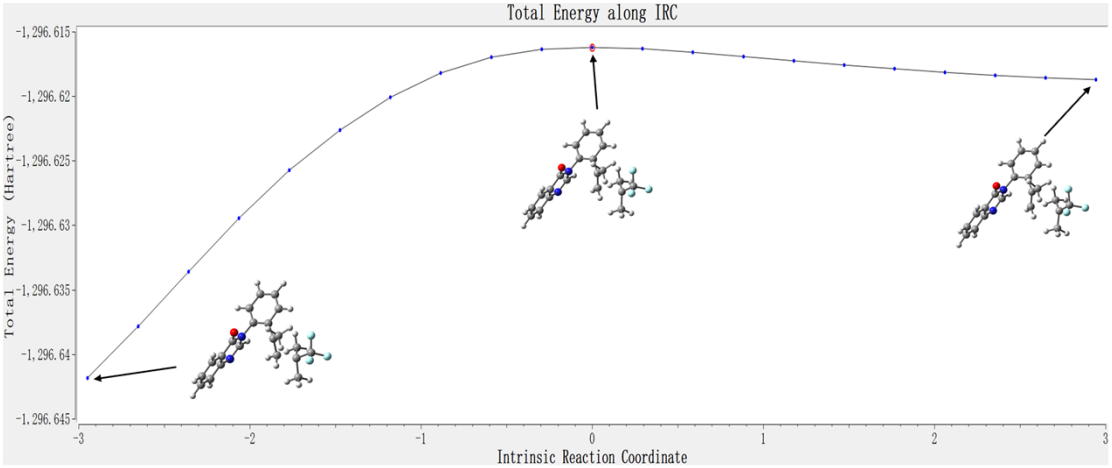


Figure S2: IRC pathway for **TS1**

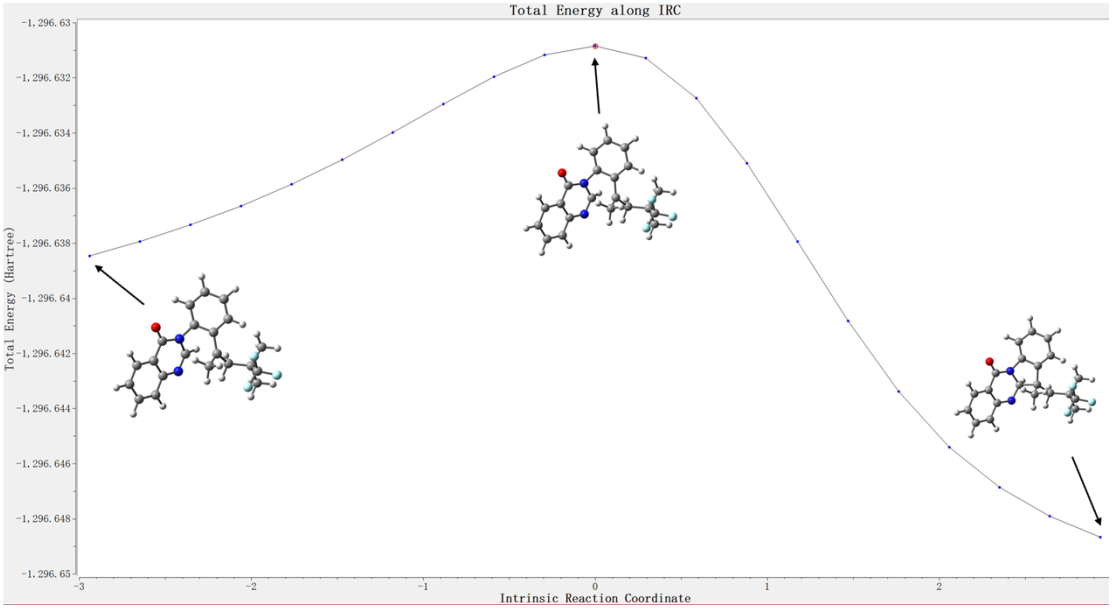


Figure S3: IRC pathway for **TS2**

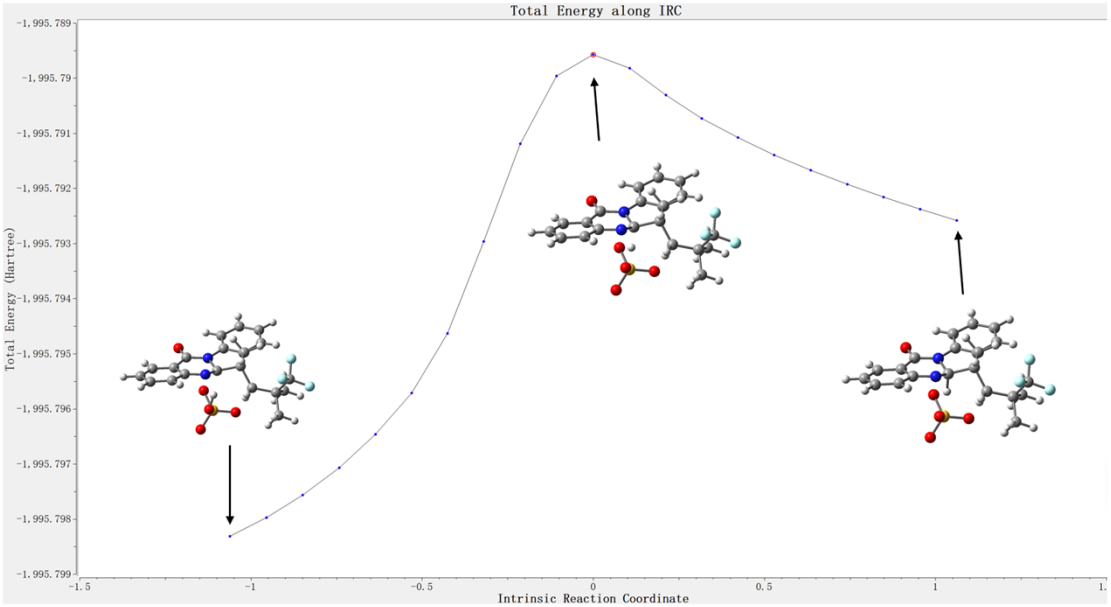
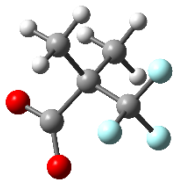


Figure S4: IRC pathway for **TS3**

3D Structure and Coordinates of all Stationary Point

2

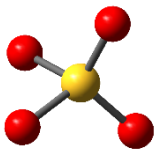


Charge: -1
Spin: 1

C	-0.27975900	0.50665400	0.00042700
C	-0.37752500	1.38391700	1.26046900
H	-0.26905400	0.78359000	2.16998900
H	0.39088800	2.16476900	1.26882300
H	-1.36328800	1.85278500	1.27504800
C	-0.37784400	1.38598400	-1.25813100
H	0.39060800	2.16680000	-1.26548400
H	-0.26972300	0.78712900	-2.16867100
H	-1.36361000	1.85485500	-1.27156200
C	1.06724900	-0.19678600	-0.00032400
F	1.27270400	-0.97356900	1.08978300
F	2.09973100	0.70718200	-0.00047700
F	1.27171100	-0.97281400	-1.09116400
C	-1.48278200	-0.52150300	-0.00015000
O	-1.20801000	-1.74563100	0.00066200
O	-2.61813500	0.01979200	-0.00130800

Zero-point correction=
0.110742 (Hartree/Particle)
Thermal correction to Energy=0.120796
Thermal correction to Enthalpy=0.121740
Thermal correction to Gibbs Free Energy=
0.073915
Sum of electronic and zero-point Energies=
-644.188556
Sum of electronic and thermal Energies=
-644.178503
Sum of electronic and thermal Enthalpies=
-644.177559
Sum of electronic and thermal Free Energies=
-644.225384
E（B3LYP-(D3)/6-311++G(d,p)）=
-644.299299

SO_4-·

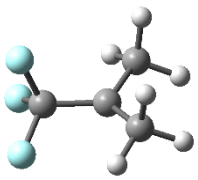


Charge: -1
Spin: 2

S	0.08127600	-0.00009700	-0.00033600
O	0.88279500	1.24150700	-0.00468000
O	0.88790700	-1.23797400	0.00509200
O	-0.96659100	-0.00704100	-1.12746600
O	-0.96666400	0.00370200	1.12772700

Zero-point correction=0.014059
(Hartree/Particle)
Thermal correction to Energy=0.018498
Thermal correction to Enthalpy=0.019442
Thermal correction to Gibbs Free Energy=
-0.014330
Sum of electronic and zero-point Energies=
-699.115619
Sum of electronic and thermal Energies=
-699.111180
Sum of electronic and thermal Enthalpies=
-699.110236
Sum of electronic and thermal Free Energies=
-699.144008
E（B3LYP-(D3)/6-311++G(d,p)）=
-699.129678

C-radical

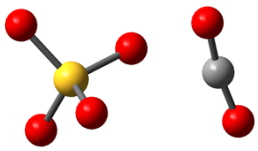


Charge: 0
Spin: 2

C	0.84994000	0.00000000	-0.16403900
C	1.57586300	1.29568900	-0.01464700
H	0.98860600	2.13998200	-0.38471100
H	1.81450600	1.49721500	1.04335800

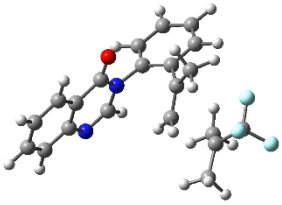
H 2.52975900 1.26543400 -0.55273200
C 1.57582500 -1.29571000 -0.01464800
H 1.81454200 -1.49719900 1.04334700
H 0.98850800 -2.13999500 -0.38463400
H 2.52968100 -1.26551700 -0.55280700
C -0.62724100 0.00000900 -0.02213900
F -1.20531500 1.09022900 -0.58447600
F -1.02400100 -0.00012100 1.28928000
F -1.20534200 -1.09009100 -0.58469100
Zero-point correction=0.094699
(Hartree/Particle)
Thermal correction to Energy=0.102917
Thermal correction to Enthalpy=0.103861
Thermal correction to Gibbs Free Energy=
0.059578
Sum of electronic and zero-point Energies=
-455.444369
Sum of electronic and thermal Energies=
-455.436152
Sum of electronic and thermal Enthalpies=
-455.435207
Sum of electronic and thermal Free Energies=
-455.479490
E（B3LYP-(D3)/6-311++G(d,p)）=
-455.539069

SO_4^{2-}+CO_2



Charge: -2
Spin: 1
C 2.21566300 0.00666000 -0.00016500
O 2.35230700 -1.15689900 0.00007000
O 2.28536600 1.17650500 0.00004100
S -1.05289200 -0.00319900 0.00000500
O -1.81503500 1.30697500 -0.00092200
O -0.17683300 -0.08044400 1.23955600
O -0.17487800 -0.08106100 -1.23812400
O -2.02689100 -1.16367300 -0.00050700
Zero-point correction=0.027887
(Hartree/Particle)
Thermal correction to Energy=0.035872
Thermal correction to Enthalpy=0.036816
Thermal correction to Gibbs Free Energy=
-0.006408
Sum of electronic and zero-point Energies=
-887.867413
Sum of electronic and thermal Energies=
-887.859428
Sum of electronic and thermal Enthalpies=
-887.858483
Sum of electronic and thermal Free Energies=
-887.901707
E（B3LYP-(D3)/6-311++G(d,p)）=
-887.895300

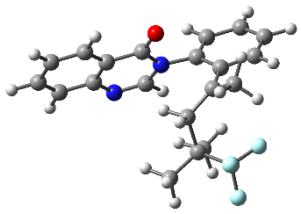
TS1



Charge: 0
Spin: 2
C -5.35990000 -2.00586400 -0.07777200
C -4.55721500 -1.58353800 -1.12627900
C -3.50603600 -0.67756900 -0.89160700
C -3.28593800 -0.20842600 0.42452300
C -4.10768600 -0.64318900 1.47735000
C -5.13742000 -1.53671900 1.22991800
H -6.16835200 -2.70557900 -0.26750200
H -4.71660800 -1.93674300 -2.13981800
C -2.20000400 0.73443600 0.69051300
H -3.91399100 -0.26552000 2.47545300
H -5.77242900 -1.87536000 2.04239600
C -1.75409400 0.54554700 -1.69820000
H -1.09507300 0.88006500 -2.49456800
O -1.93262400 1.22075200 1.78471900
N -2.71539200 -0.27469100 -1.96100400
N -1.44669900 1.05944600 -0.45600400
C -0.31346200 1.93668800 -0.32493100
C 0.81775900 1.52855100 0.40940900
C -0.37903700 3.18668000 -0.93644100
C 1.86992700 2.45322100 0.52254400
C 0.69417900 4.07141500 -0.83580900
H -1.27935200 3.46437400 -1.47558800

C 1.81824500 3.70041700 -0.09780200
H 2.75809500 2.17083600 1.07609900
H 0.64370700 5.04223600 -1.31814400
H 2.65923600 4.38094700 -0.00512700
C 0.92386600 0.19727000 1.05072700
C 0.68007200 -0.95057000 0.35557700
H 0.67733900 -1.90432500 0.87258500
H 0.20854400 -0.93719300 -0.61909600
C 1.40586900 0.15672400 2.47637400
H 2.42117300 0.55695300 2.57839700
H 0.75012200 0.76201500 3.11337100
H 1.41600200 -0.86868100 2.85424700
C 2.59899700 -1.55419100 -0.86218200
C 2.23263300 -2.96006900 -1.24116400
H 1.27391900 -2.97570000 -1.77017100
H 2.98537900 -3.39358500 -1.91831700
H 2.15743200 -3.61249600 -0.36666100
C 2.61884700 -0.51648600 -1.94589100
H 2.68289300 0.49589300 -1.54010200
H 3.47820400 -0.66499300 -2.61925300
H 1.71255200 -0.58874100 -2.55595300
C 3.66337900 -1.43673300 0.17011200
F 3.38687700 -2.13799600 1.29897000
F 3.90020000 -0.15499200 0.54765700
F 4.86613800 -1.91915500 -0.27937900
Zero-point correction=0.368049 (Hartree/Particle)
Thermal correction to Energy=0.392617
Thermal correction to Enthalpy=0.393562
Thermal correction to Gibbs Free Energy= 0.311705
Sum of electronic and zero-point Energies= -1296.248170
Sum of electronic and thermal Energies= -1296.223601
Sum of electronic and thermal Enthalpies= -1296.222657
Sum of electronic and thermal Free Energies= -1296.304513
E（B3LYP-(D3)/6-311++G(d,p)）= -1296.616218
Imagiinary frequencies= -290.48

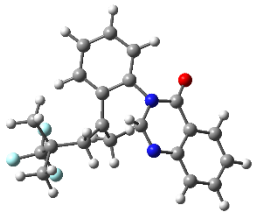
TS1-int



Charge: 0
Spin: 2
C 5.20520800 1.66448700 0.04000600
C 4.42317800 1.26490200 -1.03276300
C 3.31695100 0.42048500 -0.82468400
C 3.01966000 -0.01053200 0.48926700
C 3.82266700 0.39880700 1.56676900
C 4.90733800 1.23194300 1.34537300
H 6.05662400 2.31694300 -0.12880900
H 4.64125900 1.58880500 -2.04511500
C 1.87365400 -0.88724100 0.72895600
H 3.57006000 0.05129900 2.56259800
H 5.52719000 1.55216300 2.17675700
C 1.53059900 -0.71897100 -1.67822200
H 0.89586700 -1.04337000 -2.49708600
O 1.54369100 -1.34253900 1.81862400
N 2.55151700 0.03310400 -1.91772900
N 1.12600400 -1.16778700 -0.43661200
C -0.04366600 -2.00073000 -0.34291800
C -1.17214600 -1.60930100 0.43230300
C 0.00328700 -3.22367900 -1.00648900
C -2.21551400 -2.56975000 0.51912900
C -1.06473800 -4.11774000 -0.93573600
H 0.90114900 -3.48302700 -1.55918000
C -2.17372800 -3.78302700 -0.15460700
H -3.09776100 -2.32239700 1.09794500
H -1.01795500 -5.06515300 -1.46239000
H -3.01239800 -4.46828300 -0.07468400
C -1.32725200 -0.35308600 1.13079700
C -0.80694300 0.96800000 0.63188800
H -0.74143800 1.65710000 1.47942400
H 0.20183400 0.88917900 0.22463500
C -2.17916200 -0.32541500 2.37097900
H -3.24641500 -0.18805100 2.14750600
H -2.08305600 -1.25244600 2.94508000
H -1.88525100 0.50986600 3.01447000
C -1.62381000 1.68976200 -0.49487000
C -1.00423200 3.08507900 -0.69645400

H 0.05851200 2.97691600 -0.93342700
H -1.48697100 3.61626400 -1.52101200
H -1.09264800 3.69357800 0.20887600
C -1.58998200 0.90810400 -1.81687400
H -1.93723600 -0.11946900 -1.69140600
H -2.21667000 1.39625700 -2.56943900
H -0.56602500 0.88801400 -2.19888100
C -3.08087700 1.86689300 -0.07682300
F -3.19954900 2.40928400 1.16020200
F -3.76645100 0.69563600 -0.05947600
F -3.75442100 2.68341000 -0.92457100
Zero-point correction=0.372524
(Hartree/Particle)
Thermal correction to Energy=0.396243
Thermal correction to Enthalpy=0.397187
Thermal correction to Gibbs Free Energy=
0.317857
Sum of electronic and zero-point Energies=
-1296.285536
Sum of electronic and thermal Energies=
-1296.261818
Sum of electronic and thermal Enthalpies=
-1296.260873
Sum of electronic and thermal Free Energies=
-1296.340203
E（B3LYP-(D3)/6-311++G(d,p)）=
-1296.658060

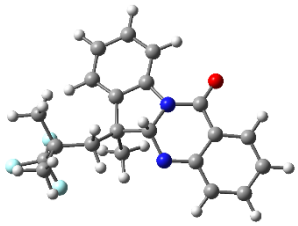
TS2



Charge: 0
Spin: 2
C 4.61198600 -2.80091600 -0.24270500
C 3.40862600 -2.64941000 0.42495200
C 2.81477100 -1.37091700 0.55053800
C 3.48255900 -0.25185600 -0.02234600
C 4.69965300 -0.42364900 -0.69126300
C 5.26607700 -1.68764400 -0.80291300
H 5.05691800 -3.78739400 -0.33318600
H 2.89542400 -3.49630000 0.86868600
C 2.85898000 1.07945200 0.02253200
H 5.18092700 0.44818000 -1.12117100
H 6.21087800 -1.81726300 -1.32098200
C 1.05627100 -0.06028500 1.26754900
O 3.32982200 2.08349400 -0.50865300
N 1.65083900 -1.24954400 1.25936100
N 1.63409700 1.10600900 0.69398500
C 0.63962100 2.07778700 0.38418000
C -0.60871500 1.50714500 0.05422600
C 0.85918000 3.45081000 0.36822600
C -1.63102600 2.36774900 -0.35319700
C -0.19104200 4.28990500 -0.01034400
H 1.82981700 3.84681400 0.63548200
C -1.42428800 3.75050000 -0.37670800
H -2.57456700 1.96350700 -0.69282300
H -0.03917700 5.36472800 -0.02563100
H -2.23146600 4.40431000 -0.69271900
C -0.64671400 0.00483500 0.07037400
C -1.59241200 -0.79703800 0.95206200
H -1.15757900 -1.80122700 0.99749600
H -1.54379300 -0.39508000 1.97010400
C -0.15923900 -0.63327400 -1.20877800
H -0.88217500 -0.47864400 -2.01687200
H 0.78397000 -0.18180100 -1.53417700
H -0.00832400 -1.70863500 -1.08017800
C -3.12908100 -0.97141200 0.69357500
C -3.56541900 -2.23931200 1.45883800
H -3.26823700 -2.14748900 2.50758000
H -4.65056400 -2.36657400 1.42010100
H -3.09253500 -3.13500400 1.04582200
C -3.94015800 0.22344100 1.22631500
H -3.61303900 1.17594800 0.81163000
H -5.00445300 0.09644800 1.00824900
H -3.82082600 0.27448500 2.31266500
C -3.45272800 -1.19093300 -0.77775300
F -2.73517700 -2.20713000 -1.31417700
F -3.20561300 -0.09258400 -1.54197600
F -4.75842200 -1.49361000 -0.96926700
H 0.44717000 0.16782700 2.14033300
Zero-point correction=0.372105
(Hartree/Particle)
Thermal correction to Energy=0.394847
Thermal correction to Enthalpy=0.395791

Thermal correction to Gibbs Free Energy= 0.320639
Sum of electronic and zero-point Energies= -1296.258738
Sum of electronic and thermal Energies= -1296.235996
Sum of electronic and thermal Enthalpies= -1296.235052
Sum of electronic and thermal Free Energies= -1296.310204
E（B3LYP-(D3)/6-311++G(d,p)）= -1296.630843
Imagiinary frequencies= -488.43

TS2-int

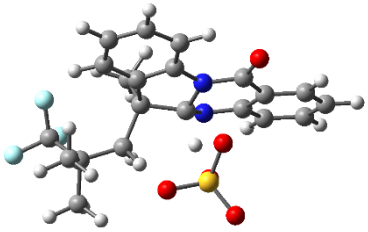


Charge: 0
Spin: 2

C	4.86460800	-2.72488600	-0.25749500
C	3.49486800	-2.68653400	-0.08395600
C	2.82018300	-1.44336100	0.12175700
C	3.60286400	-0.23703800	0.10879400
C	4.97880300	-0.30252600	-0.06978600
C	5.61626800	-1.53448600	-0.24401600
H	5.36607900	-3.67678800	-0.40156500
H	2.89467000	-3.59027600	-0.08212000
C	2.93930100	1.08655600	0.18102300
H	5.54292700	0.62367500	-0.08308700
H	6.69246100	-1.57169000	-0.37788100
C	0.86142100	-0.24256800	0.65285600
O	3.54603900	2.15213200	0.04004600
N	1.49949400	-1.47001600	0.33279900
N	1.58472100	1.00788300	0.35035000
C	0.63976700	2.03890800	0.19358400
C	-0.64155900	1.48465200	0.00719100
C	0.87223200	3.41338300	0.17073900
C	-1.69819100	2.34129100	-0.28445800
C	-0.21768600	4.25409400	-0.07147300
H	1.87009600	3.79989700	0.32168600
C	-1.48795700	3.72598000	-0.30654300
H	-2.67539600	1.94788100	-0.52620100
H	-0.06519200	5.32921000	-0.08955200
H	-2.32100500	4.38887000	-0.51990200
C	-0.55553200	-0.04224100	-0.01482100
C	-1.50833000	-0.90473100	0.86135700
H	-1.12652000	-1.92449300	0.73952500
H	-1.30887000	-0.63842900	1.90549500
C	-0.46160300	-0.50706000	-1.48324200
H	-1.34486700	-0.21143700	-2.04706600
H	0.41125100	-0.04711600	-1.95878400
H	-0.34980800	-1.59308600	-1.53730300
C	-3.06385400	-0.98957300	0.80431700
C	-3.44504200	-2.28890500	1.55358700
H	-2.98459400	-2.28079100	2.54564300
H	-4.52793000	-2.36718600	1.67908600
H	-3.08935900	-3.17448300	1.01873500
C	-3.73873300	0.19178200	1.52680400
H	-3.42860000	1.16045900	1.13882900
H	-4.82781300	0.11922600	1.45373700
H	-3.46842900	0.15600000	2.58651400
C	-3.62867200	-1.11504400	-0.60493900
F	-3.02652100	-2.09954000	-1.31374200
F	-3.50713500	0.02577300	-1.33607300
F	-4.95330500	-1.40208400	-0.59265300
H	0.70680100	-0.25506700	1.74632200

Zero-point correction= 0.374649 (Hartree/Particle)
Thermal correction to Energy= 0.397289
Thermal correction to Enthalpy= 0.398233
Thermal correction to Gibbs Free Energy= 0.323387
Sum of electronic and zero-point Energies= -1296.279782
Sum of electronic and thermal Energies= -1296.257143
Sum of electronic and thermal Enthalpies= -1296.256198
Sum of electronic and thermal Free Energies= -1296.331045
E（B3LYP-(D3)/6-311++G(d,p)）= -1296.654432

TS3



Charge: -1

Spin: 3

C 4.74237700	-2.73614800	-1.23175500
C 3.36202300	-2.71441500	-1.32884900
C 2.63654600	-1.51141100	-1.06974200
C 3.38580700	-0.31329400	-0.79625200
C 4.76873300	-0.35466000	-0.72884200
C 5.45338100	-1.56467300	-0.91996700
H 5.28083000	-3.66342900	-1.39979300
H 2.79253300	-3.60816500	-1.56010600
C 2.68212200	0.98732700	-0.76031400
H 5.31287900	0.56591700	-0.54639600
H 6.53565200	-1.58755600	-0.85064100
C 0.65508600	-0.38713200	-0.56274900
O 3.24987300	2.07251500	-0.78071200
N 1.30048800	-1.54648300	-1.08840900
N 1.29206000	0.86883300	-0.80311200
C 0.34843400	1.89268800	-0.90819100
C -0.94153600	1.32622500	-0.94291800
C 0.57399100	3.26815300	-1.01924100
C -2.02730000	2.16426600	-1.17551200
C -0.53729800	4.08804300	-1.19889800
H 1.57709300	3.66542700	-0.97145000
C -1.82407000	3.54309900	-1.29108500
H -3.02155900	1.75659500	-1.29182900
H -0.39784200	5.16121400	-1.28452200
H -2.67484300	4.19497700	-1.46331200
C -0.85833800	-0.19218400	-0.87246900
C -1.60931100	-0.94792900	0.26983500
H -1.33167900	-1.99786500	0.12114400
H -1.14327100	-0.64304600	1.20661900
C -1.14743400	-0.77245400	-2.28050200
H -2.15506500	-0.51154400	-2.60144800
H -0.43868800	-0.36318700	-3.00745400
H -1.04255700	-1.85932500	-2.27164800
C -3.12627400	-0.91480700	0.61199800
C -3.33355900	-2.06499800	1.62784900
H -2.64325600	-1.92804300	2.46487800
H -4.35395300	-2.06547400	2.01930200
H -3.13276600	-3.03974600	1.17310400
C -3.54434000	0.39893600	1.29838400
H -3.45378000	1.26717500	0.64826500
H -4.58007200	0.33710000	1.64643600
H -2.89145300	0.56072800	2.16025000
C -4.04106300	-1.19951800	-0.57106400
F -3.65796100	-2.30021200	-1.26219700
F -4.09663300	-0.17786400	-1.47093300
F -5.32276900	-1.41009300	-0.18317500
H 0.82167300	-0.60102300	0.71708200
S 1.04851900	0.37981000	2.82416300
O -0.39884900	0.61425800	3.10166300
O 1.82279100	0.01174400	4.04318700
O 1.66833600	1.48828600	2.04049800
O 1.15839600	-0.93071400	1.90711500

Zero-point correction=0.385001 (Hartree/Particle)

Thermal correction to Energy=0.413337

Thermal correction to Enthalpy=0.414281

Thermal correction to Gibbs Free Energy= 0.325531

Sum of electronic and zero-point Energies= -1995.404569

Sum of electronic and thermal Energies= -1995.376233

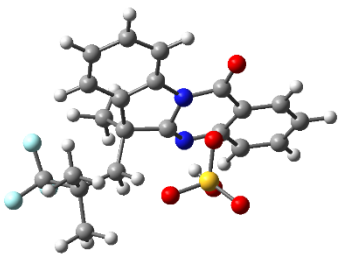
Sum of electronic and thermal Enthalpies= -1995.375289

Sum of electronic and thermal Free Energies= -1995.464039

E（B3LYP-(D3)/6-311++G(d,p)）= -1995.789570

Imagiinary frequencies= -1230.57

TS3-pro

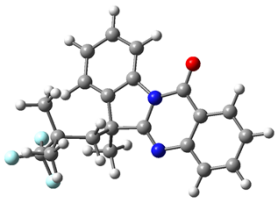


Charge: -1
Spin: 3

C	4.74747500	-2.56980300	-1.52159800
C	3.37727400	-2.55349400	-1.66729000
C	2.61449200	-1.37979500	-1.31002200
C	3.35266900	-0.19910800	-0.88909600
C	4.72414200	-0.24042700	-0.77609100
C	5.43547600	-1.42627500	-1.06500500
H	5.30596400	-3.46867800	-1.76343500
H	2.82720100	-3.42265100	-2.01163000
C	2.62597400	1.08357400	-0.72036400
H	5.25377800	0.65887400	-0.47933000
H	6.51447900	-1.44562700	-0.95859200
C	0.61134800	-0.30127300	-0.84570400
O	3.18578500	2.16586000	-0.57096500
N	1.29737200	-1.42668100	-1.35323000
N	1.24798300	0.95941200	-0.82039300
C	0.28537300	1.98556000	-0.80287400
C	-0.99151400	1.41109400	-0.94509000
C	0.48600700	3.36350700	-0.71924000
C	-2.08868000	2.25389600	-1.09188300
C	-0.63792500	4.18446100	-0.81896000
H	1.47938000	3.76844300	-0.59195700
C	-1.91075500	3.63956600	-1.01892800
H	-3.07400100	1.84482400	-1.27298100
H	-0.51478000	5.26148100	-0.75643400
H	-2.76966100	4.29552700	-1.12259400
C	-0.89150700	-0.10876900	-1.04238600
C	-1.55118500	-0.96302700	0.09714000
H	-1.28586100	-1.99668500	-0.15256400
H	-1.01747700	-0.72348700	1.01798000
C	-1.29015000	-0.58293000	-2.46259400
H	-2.33062500	-0.34239800	-2.67835300
H	-0.66113900	-0.08785100	-3.20940900
H	-1.14853100	-1.66266300	-2.55333600
C	-3.03777200	-0.96220900	0.56001600
C	-3.15577000	-2.16380200	1.52927200
H	-2.40843400	-2.05150100	2.31972500
H	-4.14572400	-2.20127400	1.99110600
H	-2.97489100	-3.11203000	1.01373000
C	-3.41136600	0.31178400	1.33997800
H	-3.37739900	1.20996600	0.72601300
H	-4.41764200	0.22050900	1.76125000
H	-2.69723700	0.43558500	2.15844900
C	-4.03681900	-1.19242600	-0.56517900
F	-3.69521800	-2.24423400	-1.34853600
F	-4.17302500	-0.12010700	-1.39482600
F	-5.28319500	-1.44677100	-0.09523500
H	1.06386600	-0.87236200	1.03688200
S	1.09985800	0.12384900	2.96048000
O	-0.37123500	0.02093900	3.15590800
O	1.89740300	-0.24519100	4.14823300
O	1.52029300	1.37391900	2.28354400
O	1.49097200	-1.09794300	1.90027000

Zero-point correction=0.388681
(Hartree/Particle)
Thermal correction to Energy=0.417929
Thermal correction to Enthalpy=0.418873
Thermal correction to Gibbs Free Energy=
0.327760
Sum of electronic and zero-point Energies=
-1995.413588
Sum of electronic and thermal Energies=
-1995.384340
Sum of electronic and thermal Enthalpies=
-1995.383396
Sum of electronic and thermal Free Energies=
-1995.474510
E（B3LYP-(D3)/6-311++G(d,p)）=
-1995.802269

3aa



Charge: 0
Spin: 1

C	5.01230900	-2.53625400	-0.14276500
C	3.65268600	-2.51927300	-0.41394000
C	2.91539000	-1.33053000	-0.26421200
C	3.58348300	-0.15795700	0.16520900
C	4.96141000	-0.19046000	0.43632300
C	5.67268700	-1.36987800	0.28430300
H	5.57238200	-3.45905800	-0.26094600
H	3.12954600	-3.41105000	-0.74329200
C	2.84318500	1.09646800	0.32237200

H 5.44607000 0.72323400 0.76302200
H 6.73734700 -1.39532100 0.49369700
C 0.91739400 -0.23781000 -0.39698900
O 3.32627900 2.16766200 0.68428000
N 1.55298200 -1.34757000 -0.54083600
N 1.48421300 0.96649600 0.00821800
C 0.50195900 1.99686800 -0.00810200
C -0.72825800 1.44391900 -0.39269500
C 0.67142500 3.35498600 0.24224900
C -1.81269900 2.28942600 -0.59598400
C -0.44352500 4.18186100 0.07043900
H 1.63290400 3.74469600 0.54293500
C -1.66725900 3.66081700 -0.35537700
H -2.76197200 1.89483600 -0.93565200
H -0.34506000 5.24681300 0.25752700
H -2.51465200 4.32268700 -0.50486900
C -0.58932600 -0.05744200 -0.60172700
C -1.20603300 -0.97508500 0.51326500
H -0.91327700 -1.98974400 0.22730800
H -0.65809200 -0.75680800 1.43664100
C -0.94707800 -0.48663400 -2.03833000
H -1.99456400 -0.29308600 -2.26110800
H -0.33617500 0.07196300 -2.75399100
H -0.74671900 -1.55317200 -2.17023500
C -2.69545900 -1.01612500 0.96230800
C -2.81316500 -2.25437100 1.88339300
H -2.07936400 -2.17551400 2.69049600
H-3.80831700 -2.31647200 2.33030400
H -2.61877200 -3.17978700 1.33301100
C -3.11752900 0.22711400 1.76525500
H -3.05114400 1.14677200 1.18650200
H -4.14501000 0.11683100 2.12495900
H -2.46245000 0.32793200 2.63582900
C -3.67057700 -1.22823600 -0.19085900
F -3.28641300 -2.23818800 -1.00742000
F -3.82156200 -0.12647900 -0.97604600
F -4.91418000 -1.53399300 0.24981200
Zero-point correction=0.364377
(Hartree/Particle)
Thermal correction to Energy=0.386781
Thermal correction to Enthalpy=0.387725
Thermal correction to Gibbs Free Energy=
0.314014

Sum of electronic and zero-point Energies=
-1295.743568
Sum of electronic and thermal Energies=
-1295.721164
Sum of electronic and thermal Enthalpies=
-1295.720220
Sum of electronic and thermal Free Energies=
-1295.793931
E（B3LYP-(D3)/6-311++G(d,p)）=
-1296.107945

VI. Reference

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